CORRELATION OF RADIOIODINE EFFICIENCIES RESULTING FROM A STANDARDIZED TEST PROGRAM FOR ACTIVATED CARBONS

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Abstract

Considerable data has been reported on the efficiency of activated carbons, both impregnated and unimpregnated, on radioiodine and its compounds. Unfortunately, the characterization of the carbons tested has been very sketchy, being limited mostly to brand names and nominal mesh size. The author's group has carried out radioisotope efficiency tests on 30 lots of carbon from five sources under both normal and post LOCI conditions. These tests demonstrate substantial lot-to-lot variance in efficiency, even of the same supplier grade. Some correlation between these efficiencies, carbon physical parameters and test parameters has been obtained.

The paper proposes a standardized test pattern for evaluating nuclear service adsorption media. This includes a system for mounting test canisters in parallel with installed carbon cells, so that media samples can be given the same exposure as the cells themselves. These canisters are removed periodically and tested with radioisotopes under post-LOCI conditions, thus demonstrating current performance of the installed cells.

I. Introduction

In spite of more recent developments (amine impregnated carbons, metal zeolites, etc.) the material almost universally specified for the removal of radioiodine is iodized activated carbon. Surprisingly, the published literature on KI/I_2 impregnated coconut shell carbon provides a very limited experimental basis for this choice.

We have attempted to gather together all published test data on KI/I_2 impregnated coconut carbons. (Refs 2,3,5-11) Tables 1 and 2 list what we have unearthed. There are more reports of tests, but in many cases, these are repetitions of the listed tests. Not only is the total number of tests small, but it appears that testing was carried out on only a sample or two from each supplier. Almost no description of the physical characteristics of the tested carbons are presented in the cited references; the assumption has apparently been made that a given manufacturer's grade will remain very constant in physical characteristics from lot to lot, and will therefore perform repeatedly as it did in the published tests.

TABLE 1   CH$_3$I-131 PENETRATIONS REPORTED IN LITERATURE
(5 cm Bed Depth)

Carbon Type	TEMP C	RH %	VEL ft/min	CO mg/m^3	PEN %	DATA SOURCE
MSA 85851	140	82	41	72	1.1	ORNL 4040, p 12
MSA 85851	138	91	44	81	2.9	ORNL 4040, p 12
MSA 85851	135	95	41	73	11.4	ORNL 4040, p 12
MSA 85851	128	100	27	93	46.0	ORNL 4040, p 12
MSA 85851	133	88	39	80	5.0	ORNL 4180, p 7
MSA 85851	132	94.3	40	6.0	1.6	ORNL TM 2728, p 21
MSA 85851	130	99	39	6.2	3.8	ORNL TM 2728, p 21
MSA 85851	131	97.9	40	6.1	3.0	ORNL TM 2728, p 21
MSA 85851	131	97.7	38	6.3	2.1	ORNL TM 2728, p 22
MSA 85851	129	101.5	40	6.1	69.3	ORNL TM 2728, p 22
MSA 85851	131	99.6	40	6.1	11.1	ORNL TM 2728, p 22
MSA 85851	131	100.2	42	5.7	12.7	ORNL TM 2728, p 23
MSA 85851	133	94.0	42	5.8	1.4	ORNL TM 2728, p 23
MSA 85851	131	96.9	40	79	6.3	ORNL TM 2728, p 27
MSA 85851	131	98.7	41	78	4.9	ORNL TM 2728, p 27
BC 727	141	83	42	70	2.1	ORNL 4040, p 13
BC 727	140	86	43	69	1.3	ORNL 4040, p 12
BC 727	137	91	45	66	7.0	ORNL 4040, p 13
BC 727	137	95	42	72	25.0	ORNL 4040, p 13
BC 727	136	82	40	79	0.4	ORNL 4180, p 8
BC 727	134	89	41	76	0.9	ORNL 4180, p 8
NACAR G601	136	81	39	81	0.6	ORNL 4180. p 11
NACAR G601	136	82	40	78	0.5	ORNL 4180, p 11
NACAR G601	134	88	41	77	1.5	ORNL 4180, p 11
NACAR G601	130	99	40	79	12.0	ORNL 4180, p 11
NACAR G601	130	99	40	78	82.7	ORNL 4180, p 11
MSA 85851	25	65	40?	~17	1.0	ORNL 4374, p 95
BC 727	25	65	40?	~17	0.3	ORNL 4374, p 95
MSA 85851	25	90	40?	~ 1.75	9.4	ORNL 4374, p 96
MSA 85851	25	90	40?	~ 7	11.2	ORNL 4374, p 96
BC 727	25	90	40?	~ 1.75	6.5	ORNL 4374, p 96
BC 727	25	90	40?	~ 7	5.2	ORNL 4374, p 96
MSA 85851	24	71	40	0.1	0.35	ORNL 3915, p 69
MSA 85851	24	71	40	0.1	0.33	ORNL 3915, p 69
MSA 85851	24	<3	40	0.1	0.03	ORNL 3915, p 69
MSA 85851	25	70	38	0.37	0.06	ORNL 3915, p 76
NACAR G601	25	76	40?	~17.5	1.1	ORNL 4374, p 95
NACAR G601	25	90	40?	~17.5	9.7	ORNL 4374, p 95
MSA 24607	25	90	40	0.5	7.33	ORNL 4647, p 243
BC 727	25?	70	40	14?	0.19	ORNL TM 1913, p 10
BC (Spec 1%)	25?	70	40	14?	1.41	ORNL TM 1913, p 10
BC (Spec 2%)	25?	70	40	14?	0.22	ORNL TM 1913, p 10
BC (Spec 3%)	25?	70	40	14?	0.18	ORNL TM 1913, p 10

TABLE 1 (continued)

UK 5% KI	25	65	40	18	2.8	ORNL 4374, p 95
UK 5% KI	25	90	40	18	9.2	ORNL 4374, p 95
SS 207B	30	100	50	0.75	3.2	Ref (9), p 408
0.5% KI	30	100	50	0.75	0.66	Ref (9), p 408
Norit RCX	30	100	50	0.75	2.5	Ref (9), p 408
Norit 0.5KI	31	100	100	100	14.8	Ref (9), p 410
0.8mm ODx3mm	30	100	100	100	18.7	Ref (9), p 410
Norit RCX	30	99	50	3	22.7	Ref (9), p 411
Norit RCX	30	99	50	3	29.0	Ref (9), p 411
Norit RCX	30	99	50	3	21.5	Ref (9), p 411

TABLE 2 I_2-131 PENETRATIONS REPORTED IN LITERATURE
(5 cm BED Depth)

Carbon Type	TEMP C	RH %	VEL ft/min	CO mg/m^3	PEN %	DATA SOURCE
MSA 85851	25	96	40	0.6	0.014	ORNL 4374, p 98
MSA 85851	25	96	40	0.07	0.005	ORNL 4374, p 98
MSA 85851	25	98	40	0.005	0.15	ORNL 4374, p 98
MSA 85851	25	96	40	0.002	0.30	ORNL 4374, p 98
MSA 85851	24	69	40	5	0.07	ORNL 3915, p 69
MSA 85851	25	98	40	93	0.053	ORNL 2040, p 9
MSA 85851	25	98	40	196	0.08	ORNL 2040, p 9
MSA 85851	25	98	40	126	0.013	ORNL 2040, p 9
MSA 85851	25	98	40	99	0.07	ORNL 2040, p 9
MSA 85851	20	100	40	30	0.51	ORNL 2040, p 11
MSA 85851	20	100	40	48	0.16	ORNL 2040, p 11
MSA 85851	138	95	40	33	0.05	ORNL 4040, p 20
MSA 85851	138	100	40	49	2.2	ORNL 4040, p 20
BC 727	25	98	40	93	0.11	ORNL 2040, p 9
BC 727	25	98	40	190	0.04	ORNL 2040, p 9
BC 727	25	98	40	126	0.03	ORNL 2040, p 9
BC 727	25	98	40	101	0.052	ORNL 2040, p 9
BC 727	25	98	40	80	0.07	ORNL 2040, p 10
BC 727	25	98	40	111	0.021	ORNL 2040, p 10
BC 727	25	98	40	42	0.007	ORNL 2040, p 10
BC 727	25	98	40	64	0.002	ORNL 2040, p 10
BC 727	20	100	40	80	0.007	ORNL 2040, p 11
BC 727	20	100	40	118	0.11	ORNL 2040, p 11
BC 727	20	100	40	39	0.10	ORNL 2040, p 11
BC 727	20	100	40	61	0.03	ORNL 2040, p 11
TS 0.5% KI	51	100	62	?	1.2	Ref (10). p 375-80
SS 207B	51	100	102	?	3.0	Ref (10), p 375-80
0.5% KI	51	100	118	?	8.0	Ref (10), p 375-80

The published test data, however, raise some serious questions about this assumption. All tests in Table 1 were made in a limited range of temperatures and velocities, for a uniform bed depth (5 cm) and a uniform specified granule size (6x16 mesh). The significant test variables are therefore relative humidity and concentration of non-radioactive contaminant. Figure 1 plots CH_3I-131 penetrations against relative humidity*, with data for concentrations less than 6.3 mg/m^3 indicated by solid symbols. Concentration may be a significant variable; if so, its effect is the exact reverse of what adsorption theory predicts. Relative humidity clearly has a strong influence on penetration. The effect of temperature is not apparent.

A similar relationship exists between I_2-131 penetration and relative humidity, but the effect of temperature is significant. (See Figure 2 which plots data from Table 2). The scatter of data points is discouraging; clearly other variables are present, either in the test method or in the samples tested. Both users and suppliers are hard pressed to establish specifications for this type of carbon based on these tests, which are very nearly the only available. After examining these data, we also began to doubt the validity of calling out a particular supplier's carbon type in response to a specified performance requirement. In 1969, we began a program to unravel the reasons for the performance variations that had been observed. A test facility was built to allow exposure of adsorption canisters to tagged gases under a wide range of temperature, pressure and humidity conditions. To date, our studies have been limited to molecular iodine (mixes of I_2-131 and I_2-;27) and to methyl iodide (mixes of CH_3I-131 and CH_3I-127), but the facility can readily accept other contaminants.

Test Facility

Figure 3 is a schematic of the test facility, Figures 4 and 5 photographs of it. Supply of the main flow is straightforward, using compressed air and a steam generator to provide conditions from ambient to a maximum of 700 kN/m^2(100 lb/in^2). This allows tests to be run at any steam air ratio up to saturated conditions at 150 C. Separate feed systems are provided for two radioactive contaminants. These can be operated simultaneously, if desired. Contaminants which are fixed gases under the test conditions are fed from the supply am-

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* The scale for RH in Figure 1, is the function:

$$X = ((100/(110 - RH) - 100/110) \qquad (RH in \%)$$

This scale is used only to make the data relationships more visible. The function probably does not express any physical relationship between the test parameters.
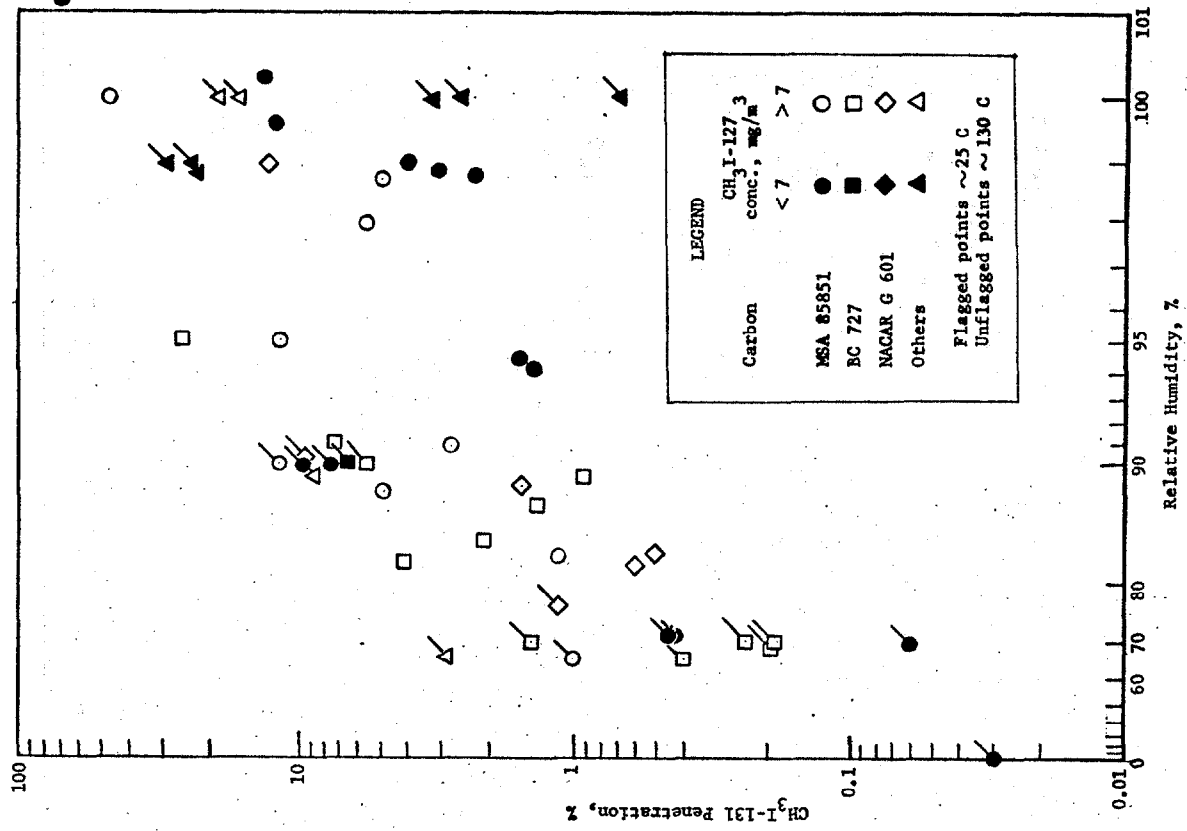
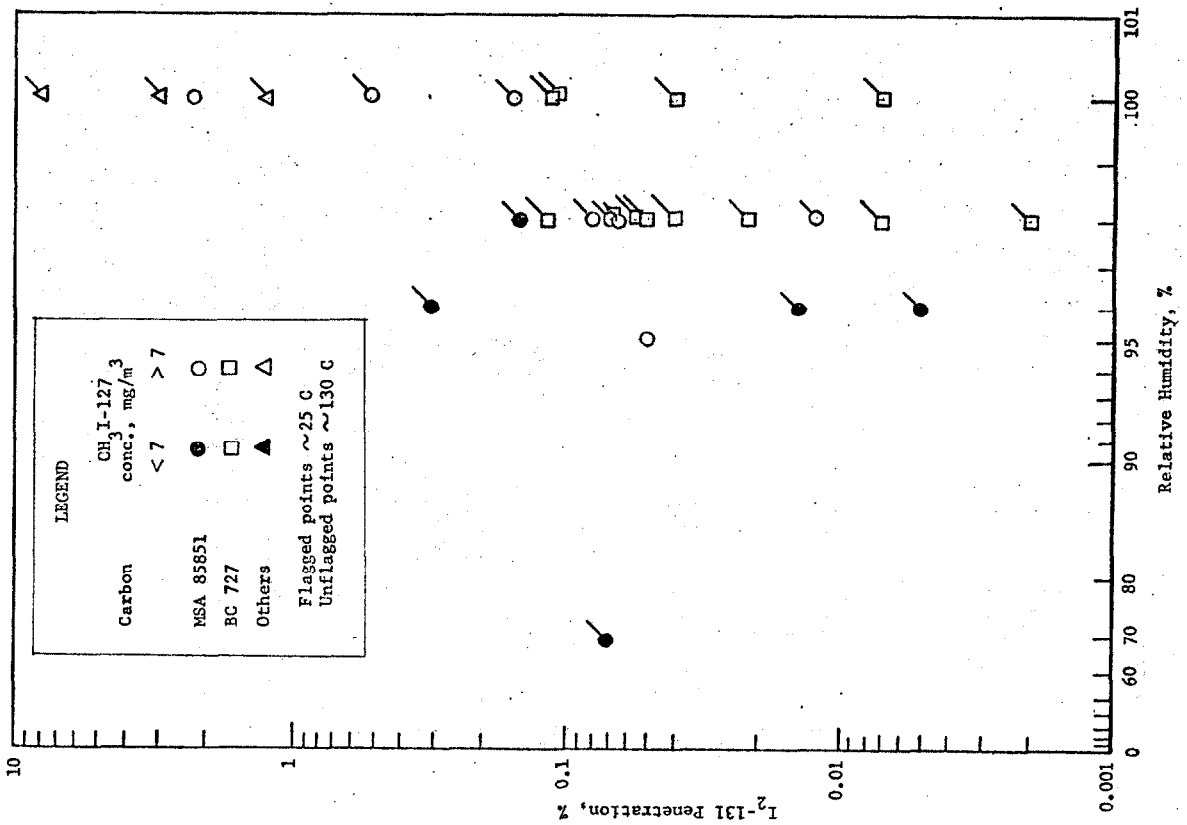FIGURE 1.   PUBLISHED PENETRATIONS,
CH$_3$I-131 vs RH
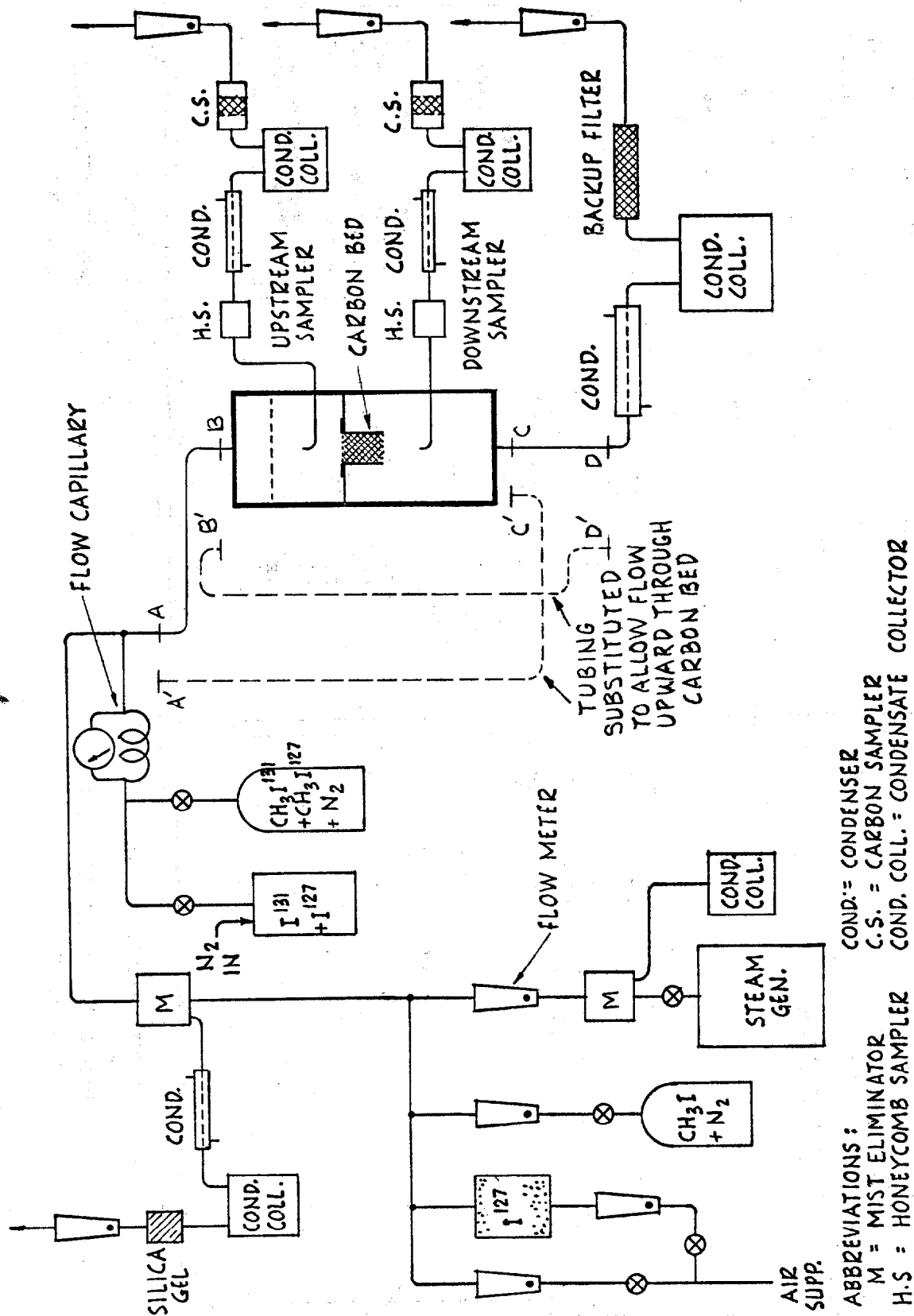

FIGURE 2.   PUBLISHED PENETRATIONS,
I$_2$-131 vs RH

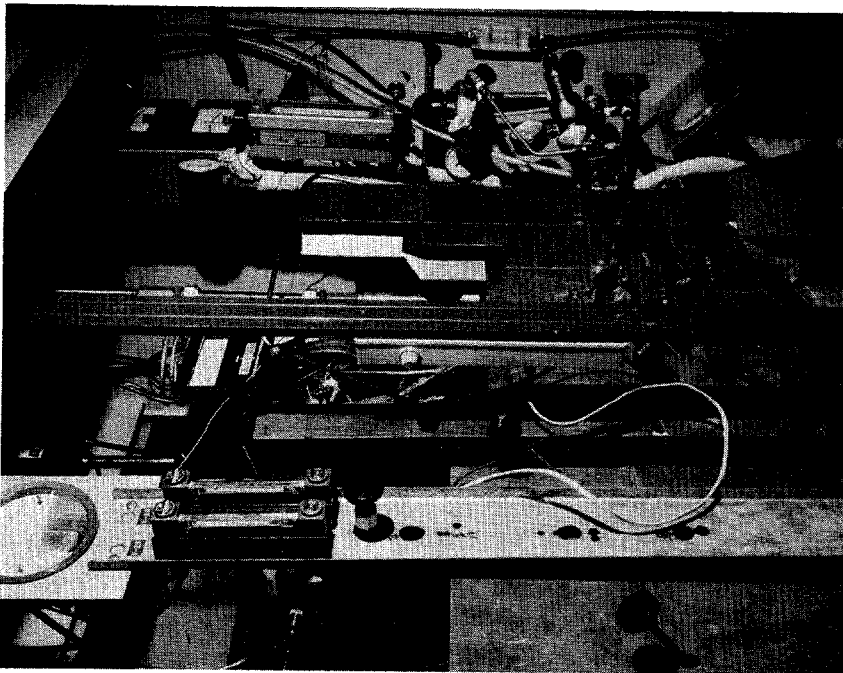FIGURE 3. SCHEMATIC OF ADSORBER/ RADIOIODINE TEST FACILITY.
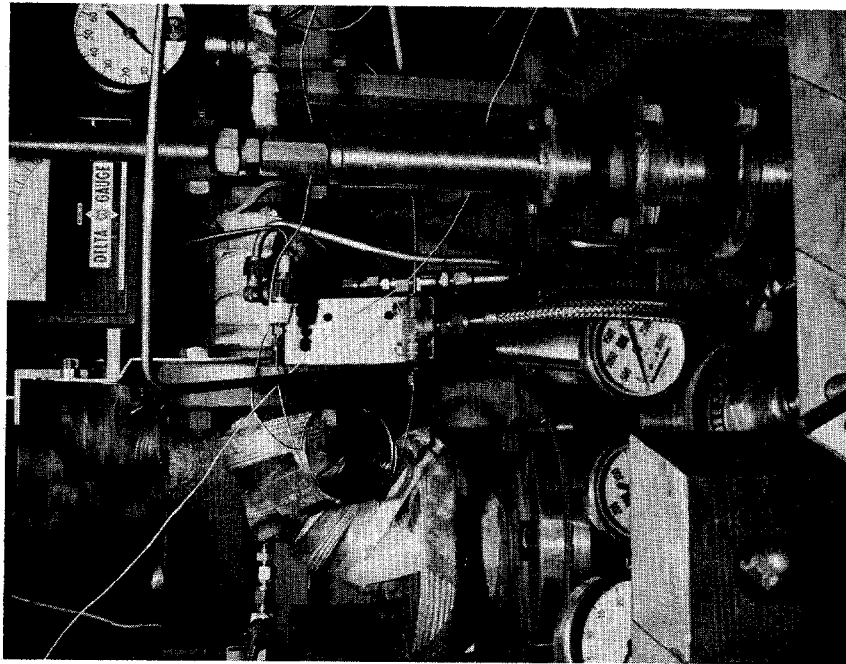
FIGURE 5. RADIOISOTOPE TEST FACILITY PRESSURE VESSEL, 'BOMB', CRUSHER

FIGURE 4. RADIOISOTOPE TEST FACILITY FRONT VIEW

poule to an evacuated storage 'bomb'. This bomb is subsequently pressurized with dry nitrogen to provide feed pressure. Molecular iodine, on the other hand, is fed directly from the supply ampoule by passing a stream of nitrogen over crystals in the bottom of the ampoule. The ampoule itself is held in a 'crusher' which allows the ampoule septum to be broken after the ampoule is sealed off inside the system.

In most tests, gamma activity of the contaminants is such that the carriers can provide a suitable amount of non-radioactive material. However, we sometimes need to feed added non-radioactive material; the system is arranged to do this.

The carbon test canister is shown in Figure 6. Flow can either be downward (in the direction of gravity) or upward (counter to gravity). In upward flow, with condensation, the bed operates under 'flooding' or 'percolating' conditions, which is generally the worst operating condition.

Downstream lie the main condenser (to eliminate steam condensate) and the primary flow filter (to remove any radiocontaminant which passes the test filter). The main flow then exhausts to the hood which surrounds the test system. A small moisture separator is in the entrance to the main stream to eliminate droplets from the flow at super-saturated conditions. This separator, with assistance from judiciously placed tape heaters, enables the system to produce conditions from essentially zero R.H. to slightly above saturation.

Sampling is carried out by two identical sampling chains, one upstream, one down. These chains (derived from the designs of Ref. 2) include, in sequence: silver plated honeycombs (to capture I_2-131); particle filters; a condenser to eliminate sampling-flow water, and assure highest efficiency performance of the following sampler carbon beds); a set of three miniature carbon canisters in series (to trap (CH_3I-131); a flowmeter; and a connection to the main flow.

Counting of activity is carried out by a NaI well-type crystal-scintillometer, using the 0.364 MeV I-131 gamma line. A single channel discriminator is used, and standard procedures followed. The contaminant feed rate is adjusted so that activity upstream is not too great to flood the counter, and activity downstream is not so low as to be statistically insignificant in relation to background.

Sampling and Efficiency Determination

Any efficiency determining method which depends on sampling may suffer from sampling errors; in this case, the potential sources of error are:
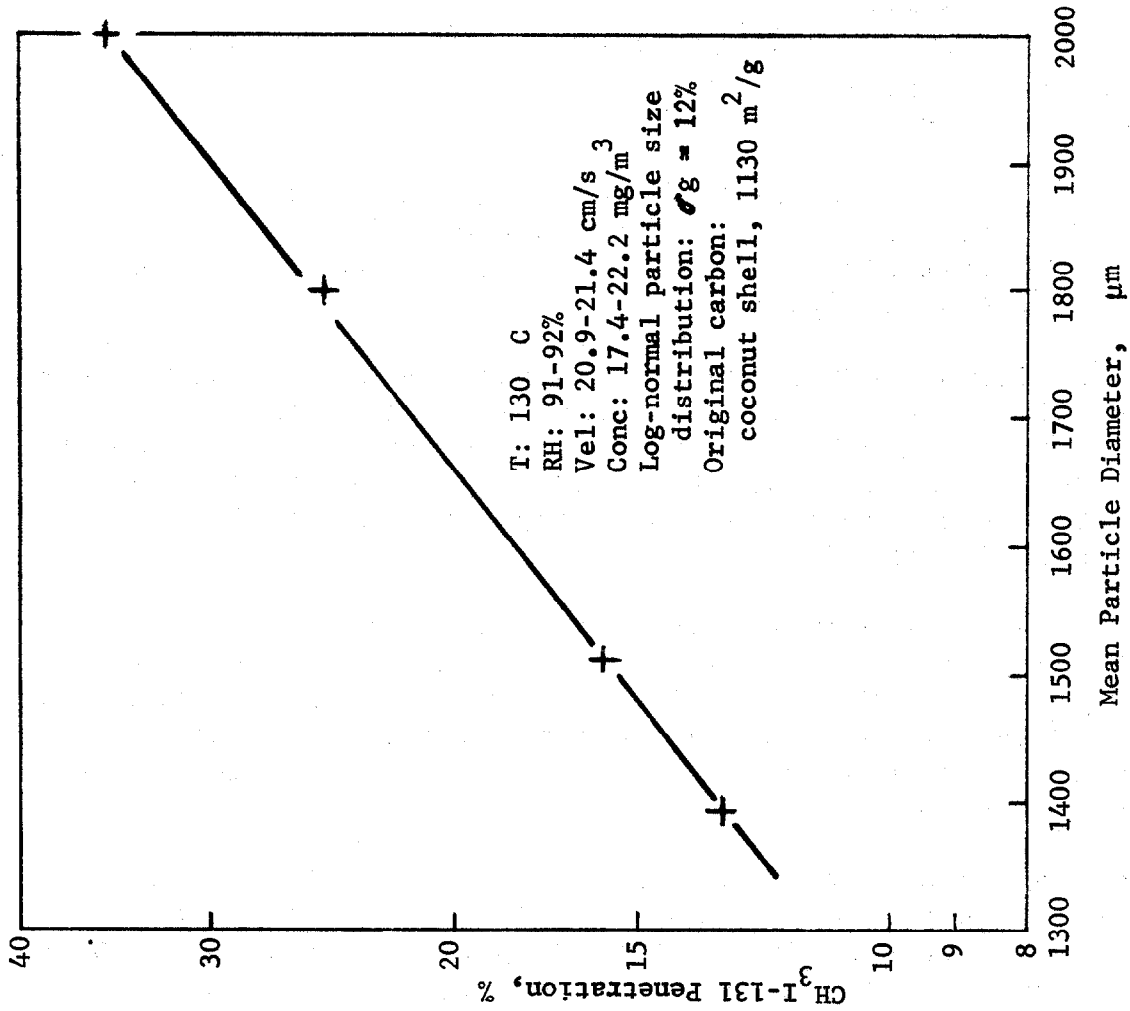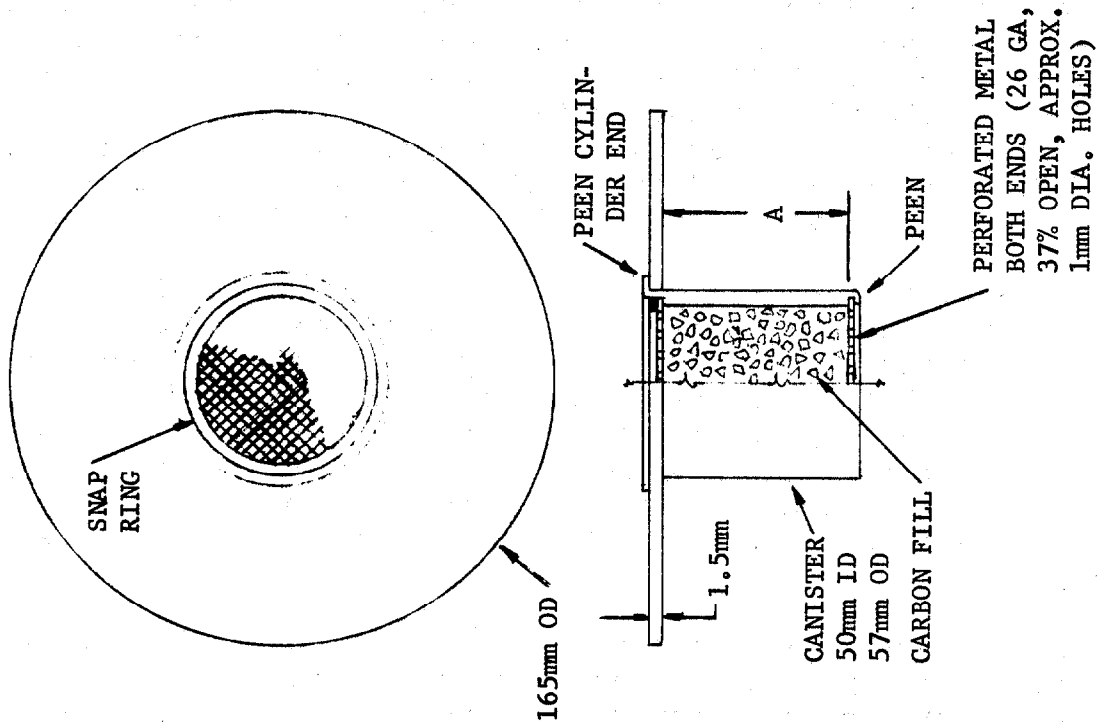
Figure 7

T: 130 C
RH: 91-92%
Vel: 20.9-21.4 cm/s
Conc: 17.4-22.2 mg/m^3
Log-normal particle size
  distribution: σ_g = 12%
Original carbon:
  coconut shell, 1130 m^2/g

CH$_3$I-131 Penetration, %

Mean Particle Diameter, μm

FIGURE 7
PENETRATION VS. PARTICLE SIZE, CH$_3$I-131

SNAP
RING

165mm OD

CANISTER
50mm ID
57mm OD

CARBON FILL

1.5mm

PEEN CYLIN-
DER END

A

PEEN

PERFORATED METAL
BOTH ENDS (26 GA,
37% OPEN, APPROX.
1mm DIA. HOLES)

FIGURE 6
STANDARD TEST CANISTER

a) sampler flow measurement
b) efficiency of sampling media
c) loss of contaminant in sampling lines or other devices
    ahead of the sampling media
d) counting errors

The decision to use samplers was based on a careful analysis of the possible error of this approach relative to whole-stream sampling and counting. The following comments explain why none of the above four items introduce significant errors:

a) Sampler flows are measured on essentially dry air downstream of the sampler line condensers. Since the ratio of steam to air is the same both upstream and downstream, this procedure allows accurate absolute measurement and control of sampler flows, and still more accurate relative measurements (which is the more important factor in efficiency calculation).

b) Since the media operates dry, efficiency is high (typically 99.7%). This is in sharp contrast to the situation with whole-stream counting, where efficiency of the 'sampling media' is unknown, variable, and often low, and one must assume purely a logarithmic decrease in concentration with bed depth in order to calculate 'de-contamination factor' or penetration.

c) Experiment showed that line losses are negligible. The sampling lines in the system are short, small diameter tubes of stainless steel, at essentially the same temperature as the main system. Counts of activity in the condensed water, and of washings from the sample lines, showed no significant activity above background. The absolute level of counts for successive runs of samples pf the same carbon under identical conditions decreases logarithmically in accordance with I-131 half-life, thus further demonstrating that there is no retention of iodine in the sample lines. The test includes a two-hour elution period after radiocontaminant injection is halted. This gas flow would scrub the sampling walls free of any temporarily adsorbed iodine, and pass it to the sampling media.

d) The sampler elements are easily inserted in a nominal 1 in ID well in an NaI scintillation crystal. Our crystal is nominal 3 in OD, the well nominal 2 in deep. Even with this much submersion, the count is about 10% lower when the sampler canister is inserted with its upstream face up, rather than down. The reason for this is that the radio contaminant is deposited in highly non-linear fashion in the sampler canister, with the bulk of the contaminant near the entrance face. Counting efficiency with the entrance face down is about 9%.

Preliminary runs showed that very little activity appeared on the silver plated honey combs or particulate filters, even when molecular iodine was the radio contaminant. Since we had no interest in

this test series in separating I_2-131 activity from CH_3I-131 activity, only carbon sampling canisters were used. The sum of activities counted in the second and third sequential sampler canisters was never greater than 1.5% of the total count.

Test Parameter Determination

The test cycle included a precondition period of 2 to 5 hours, followed by a 1 hour test run with contaminant feed, then a 2 hour post-test elution period. The same conditions of gas flow, humidity, temperature and pressure are maintained for the final half of the preconditioning period, and for the whole of the remaining periods. Pressure and temperature measurement are straightforward, using aneroid gages and thermocouples respectively. Humidity for conditions at low temperatures is determined by wet bulb/dry bulb measurement, but for high temperatures by actual weighing of water condensed in the sampling trains. Relative humidities higher than 100%, in the sense described by Ackley and Adams (Ref 2) were maintained for a few runs. If the test canister is exposed to a flow that is supersaturated, it 'floods', regardless of whether the flow is upward or downward. The degrees of flooding (the percentage of free moisture in the bed) depends on the exact conditions at the bed, on the length of the test, and on the transport of droplets from the zone ahead of the test canister. These conditions are all but impossible to control; the transport of droplets appears to be particularly erratic. We chose to remove droplets by a mist eliminator. The water removed is not included in the calculated humidity, which is based on actual vapor condensed from the gas flow at the face of the test canister.

Concentrations of non-radioactive contaminants (I_2-127 and CH_3I-127) were calculated from flow rates and mole fraction of the material in the supply feeds.

Carbon Parameter Determination

The aim of this series of tests was to establish relations between the physical parameters of the carbon and its removal efficiency for I_2-131 and CH_3I-131. Published tests gave almost no data on the parameters of the tested carbons; we were therefore obligated to find for ourselves what were the significant carbon parameters.

Particle Size. Particle size is an obvious parameter choice, since it influences the mass transfer of the contaminant from the bulk gas stream to the particle surface. We chose to evaluate particle size by dry sieving, using the method of ASTM D2862-70. Cumulative percentage of sample-vs-particle diameter plots were made on log probability paper, and the 50% size thus obtained used as the mean diameter of the sample. There was little variation in the geometric standard deviation of the particle size distributions, even though

mean sizes varied substantially.

Ref 3 includes a description of tests conducted to determine the effect of particle size on radioisotope efficiency for a carbon of this variety. There, the change in size was produced by screening off successively finer fractions of the distribution. This procedure introduces a particle size effect, but corresponds poorly with the practical case. In practice carbons are ground to at least approximately log-normal distributions having some desired mean particle diameter. We also 'constructed' some carbons of different mean sizes by recombining screened fractions, but maintained a log-normal distribution with the same standard deviation as the original sample. Results of this test series are plotted in Figure 7.

Impregnant Content. The impregnants applied to the carbons were potassium iodide and molecular iodine. It was necessary to develop an analytical procedure which would distinguish between these. A reasonably repeatable technique was developed, as follows:

Two parallel analyses are made. In the first, the carbon is mulled into a paste in a mixture of acetone and potassium iodide. (Iodide is added to improve the stability of iodine in acetone.) This paste is then vacuum filtered with additional acetone, as needed. The filtrate is titrated with sodium thiosulfate to determine content of molecular iodine (I_2) held by the carbon.

The second analysis uses 5% sodium sulfite solution in distilled water instead of acetone-KI solution during the mulling process. This dissolves both KI and I_2 impregnants. The filtration process is repeated, with added sodium sulfite solution as needed. The extract is then acidified with 50% nitric acid, and a measured excess amount of standardized silver nitrate solution plus ferric alum indicator is added. Back-titration with potassium thiocyanate then determines the total iodide (I^-) impregnant content. The content of KI and I_2 impregnants can then be calculated separately.

Carbon Surface Area. Isotopic exchange cannot take place until the exchanging molecules are in very close proximity, hence surface is an important parameter. In the limited time available to us, we chose to make use of the nitrogen-BET dynamic surface measurement (Ref 4) already available for some samples.

Some samples tested were evaluated for surface before they had been impregnated; others were available only in the impregnated form. We decided to evaluate already-impregnated carbons after leaching impregnants from them, thus putting them somewhat back to their original pre-impregnation condition. Leaching was carried out by washing the samples in boiling 10% potassium sulfite for two minutes, washing with substantial amounts of distilled water, and re-drying. The measured area is also affected by the duration of any degassing

period prior to the start of nitrogen adsorption. We made no particular effort to establish the effects of such test variations; the method did, however, distinguish clearly between high and low surface area carbons, and the correlation between surface area and efficiency was strong.

Test Results and Correlations

The results of AAF tests are listed in Tables 3 and 4. A straightforward application of multiple linear regression analysis to these data leads to some obviously unacceptable results. For example, processing the data through a multiple regression computer program gave a particle diameter exponent of 20 as a best fit, and with a very high confidence level for this variable. This is the result of a narrow data range for this parameter, rather than a valid effect. Both particle size and face velocity suffered from this defect - a narrow range for the parameter - and we therefore decided to 'force' their effects to power functions established independently.

The correlation procedure is as follows:
We assume that penetration (1-efficiency) is a function of the form:

$$P = \exp\left[f_1(T)f_2(RH)f_3(CI, CK)f_4(S)f_5(C)f_6(V)f_7(D)\right] \tag{1}$$

where:

T = temperature of the bed, K
RH = gas relative humidity, %
S = surface area of carbon, m^2/g
C = non-radioactive contaminant concentration, mg/m^3
V = face velocity, cm/min
D = carbon mean particle diameter, μm
CI = amount of Iodine impregnant, % by weight
CK = amount of Potassium Iodide impregnant, % by weight

The form of the various functions must be assumed. It seemed reasonable to assume that the effects of T, S, C, V and D could be expressed as power functions. It was also probable that CI and CK did not act independently, but combined, and that the important impregnant factor was the total iodide ion present. If this were true, then a reasonable assumption is that

$$f_3(CI, CK) = (CI + 0.765\ CK)^{m_3} \tag{2}$$

Where m_3 is a yet undetermined exponent. (The factor 0.765 corrects for the amount of I^- present in KI relative to that present in I_2.)

TABLE 3. AAF TESTS ON NUCLEAR CARBONS; CH_3I-131 PENETRATION

Temp	RH	P	Vel.	Non-Radio Conc.	Mean Part. Diam	N_2 BET Surf.	Impregnant I_2	KI	Pen.
C	%	psia	cm/s	mg/m³	μm	m²/g	%	%	%
25	80	22	20	17.5	1690	–	4.1	2.0	0.3
25	80	22	20	17.5	1834	766	0.4	1.5	0.4
128	96	55	20	6.0	1678	–	2.3	3.3	3.1
135	90	55	20	13.5	1863	–	4.0	0.0	14.5
128	101	55	22	12.4	1690	–	4.1	2.0	4.3
128	100	55	23	10.7	1678	–	2.3	3.3	18.4
69	65	26	19	52.7	1690	–	4.1	2.0	0.071
130	95	55	23	10.2	1680	–	1.6	4.3	17.4
130	92	55	22	15.9	1830	766	0.4	1.5	43.1
130	93	55	22	47.7	1610	1130	1.6	0.0	1.0
130	94	55	22	16.5	–	–	1.8	0.7	0.6
130	92	55	22	17.1	1650	–	1.5	1.8	0.13
130	99	55	21	19.2	1650	–	1.5	1.8	13.4
130	100	55	21	34.0	1610	1130	1.6	0.0	1.3
130	101	55	22	52.9	1690	–	1.5	0.6	19.5
130	91	55	21	17.7	1680	1442	3.3	1.7	0.004
130	101	55	21	18.3	1080	1442	3.3	1.7	0.42
130	93	55	22	17.4	1500	–	0.8	0.0	15.8
130	92	55	21	18.0	2000	–	0.8	0.0	34.8
130	91	55	21	18.9	1380	–	0.8	0.0	13.1
130	87	55	19	21.3	1790	–	1.6	0.0	6.8
130	92	55	21	22.2	1790	–	0.8	0.0	24.7
130	91	55	21	29.0	1790	1130	0.7	0.0	29.9
130	91	55	20	18.8	1680	1442	2.2	3.4	0.02
130	101	55	21	19.8	1680	1442	2.2	3.4	0.02
130	100	55	20	19.7	1680	1550	1.8	2.7	0.81
130	101	55	21	19.5	1680	–	2.9	3.4	2.1
130	98	55	19	20.9	1680	–	10.0	0.0	1.5
130	104	55	22	18.4	1680	–	2.6	1.1	7.1
130	0.4	25	20	22.1	1680	1440	2.2	3.4	0.02
130	101	55	21*	64.4	1620	1440	3.5	1.4	13.6
130	106	55	24	69.9	1620	1440	3.5	1.4	15.0
130	103	55	22	69.9	1620	1440	3.5	1.4	17.8
130	105	55	23	16.0	1620	1440	3.5	1.4	17.0
130	91	55	21	17.3	1620	1440	3.5	1.4	0.14
130	96	55	20	17.9	1620	1440	3.5	1.4	0.03
130	98	55	21	17.3	1600	1550	2.4	1.2	5.3
130	100	55	20	18.6	1600	1550	2.4	1.2	24.1
25	85	25	20	18.5	1620	1442	3.5	1.4	0.04
131	99	55	23*	31.9	1600	1550	2.4	1.2	0.31
130	99	55	21*	43.2	1620	1442	3.5	1.4	0.23
20	30	27	22	20.2	1600	1550	2.4	1.2	0.07
130	99	55	25	15.0	1810	950	4.3	0.0	0.30

TABLE 3. AAF TESTS ON NUCLEAR CARBONS: CH_3I-131 PENETRATION cont.

50	42	28	18	22.3	1600	1460	3.8	4.7	0.008
50	57	29	20	19.5	1650	1425	2.3	4.1	0.05
50	59	28	20	18.0	1590	1465	3.3	4.1	0.014
50	64	28	20	18.3	1600	1460	3.4	4.7	0.016
50	65	28	20	18.5	1685	1380	3.0	5.1	2.90
50	69	28	20	19.2	1620	1440	3.4	4.4	0.038
50	65	28	20	22.3	1600	1460	3.2	5.9	0.024
50	62	28	20	27.2	1600	1460	3.7	4.2	0.028
50	61	28	20	35.4	1600	1460	3.5	4.2	0.026
130	96	55	23	14.7	1810	950	4.3	0.0	11.9

TABLE 4. AAF TESTS ON NUCLEAR CARBONS: I_2-131 PENETRATION

Temp	RH	P	Vel.	Non-Radio Conc.	Mean Part. Diam.	N_2 BET Surf	Impregnant I_2	KI	Pen.
C	%	psia	cm/s	mg/m^3	μm	m^2/g	%	%	%
70	70	25	40	50.0	1690	–	4.1	2.0	0.04
130	92	55	39	17.5	1545	–	1.6	4.3	2.18
130	101	55	21	43.4	1610	1130	1.6	0.03	7.5
130	89	55	20	58.4	1610	1130	1.6	0.03	0.19
130	90	55	21	16.0	1620	1442	3.5	1.4	0.04
130	92	55	21	29.6	1834	766	0.4	1.5	0.16
24	32	27	20	17.4	1620	1442	3.5	1.4	0.08
21	30	26	19	15.6	1600	1550	2.4	1.2	0.0014
130	98	55	21	19.7	1600	1550	2.4	1.2	0.35
130	98	55	21	19.0	1620	1442	3.5	1.4	0.32
130	101	55	23*	16.4	1600	1550	2.4	1.2	1.63
132	98	55	24*	15.6	1620	1442	3.5	1.4	1.61

*Indicates test with upward gas flow.

It is clear that $f_2(RH)$ cannot be simply a power function of RH. We therefore plotted all penetrations against RH (as in Figure 1) without regard to other parameters, and drew a curve through the general mass of points. This function is expressed as follows:

for RH $\leq$ 96.25%

$$f_2(RH) = 4.75 - 1.922 \exp[-0.446(96.25 - RH)] \tag{3}$$

and for RH $>$ 96.25%

$$f_2(RH) = 2.828 \exp[-0.277(RH - 96.25)] \tag{4}$$

We now may set P equal to:

$$P = \exp[(T)^{m_1}(CI + 0.765 \ CK)^{m_3}(S)^{m_4}(C)^{m_5}(V)^{m_6}(D)^{m_7}f_2(RH)] \tag{5}$$

Taking the logarithm of both sides twice,

$$\ln(-\ln P) = m_1\ln T + m_3\ln(CI + 0.765 \ CK) + m_4\ln S$$

$$+ m_5\ln C + m_6\ln V + m_7\ln D + \ln f_2(RH) \tag{6}$$

(The negative sign is necessary because P is always less than 1, and hence has a negative logarithm.)

Equation (6) is linear, and can therefore be treated by multiple linear regression procedures to determine the best fit values of m_1, m_2, etc. Data obtained of Figure 7 and other sources led us to use 1.91 for m_1, -0.21 for m_5, -1.0 for m_6, -1.818 for m_7, all of which had too small variation in these tests for valid use of the multiple regression program. All points were fed into a multiple regression analysis program and values obtained for m_3 and m_4. The results were disappointing, particularly in the high humidities. There is no reason why the behavior for a carbon bed that has no free water in its interstices (one below 100% RH) should be the same as for a carbon bed that is at least partly filled with water — as it is above 100% RH. The data were therefore divided into two groups, one for RH 100%, one for RH 100%, and the analysis repeated. Reasonable values for all exponents, satisfactory confidence (T-test) and multiple regression of 0.84 were obtained for the complete data set (31 tests). The final expressions for penetration, with CH_3I-127 as the non-radioactive contaminent, CH_3I-131 the radioactive, are:

for RH $\leq$ 100%,

$$P = 0.345 \exp[-2.275\times10^{-5}(T)^{1.91} \ (CI + 0.765 \ CK)^{0.815}f_2(RH)$$

$$(S/1000)^{0.558}(C)^{-0.21}(V/1000)^{-1.0}(D/1000)^{-1.818}] \tag{7}$$

and for RH > 100%,

$$P = 0.345 \exp[-1.713 \times 10^{-4}(T)^{1.91}(CI + 0.765\ CK)^{1.526}f_2(RH)$$

$$(S/1000)^{-3.772}(C)^{-0.21}(V/1000)^{-1.0}(D/1000)^{-1.818}] \tag{8}$$

(The multiplicative coefficients are the results of a manipulation which causes the correlation to pass through zero and 100% penetration in the limits, while maintaining the 'best fit' criterion to the given data.)

We have not yet obtained enough data on I_2-131 penetration to carry out a regression analysis paralleling that for CH_3I-131. Figure 8 plots the penetrations predicted by Eq (7) and (8) vs measured values. The dashed lines are the 95% confidence limits for the data. Comparison with Figure 1 shows that the inclusion of the parameters of Eq (7) and (8) has reduced the spread of penetration at a given condition by a factor of 10. Apparently other factors not included in the correlation have an influence on the performance. Nevertheless, the condition is useful in establishing quality-control limits on carbons, to establish a reasonable confidence that a desired performance can be obtained. The results also indicate several other things:

a) Above 95% RH, very slight changes in test conditions will result in drastic changes in penetration. A test used for quality control purposes, or to show degradation of carbon with service life, should be run below 95% RH.

b) Too little is known about the mechanism of removal of radioiodine compounds to rely on simulant tests. This raises quality-control problems; the tests are expensive, yet testing 50 grams of carbon from a 50,000 kilogram lot is a dubious procedure.

c) Tests at ambient temperatures and low relative humidities, even on CH_3I-131, offer so little challenge to the carbon that they do not distinguish between carbons which are useful at high temperature – high humidity conditions and those that are worthless at such conditions.

Proposed Standardized Test Procedure

The following procedures and conditions will provide a reliable specification of impregnated activated carbon for radioiodine compound adsorption. In some sections there are items enclosed in brackets (thus) from which one appropriate value should be selected.
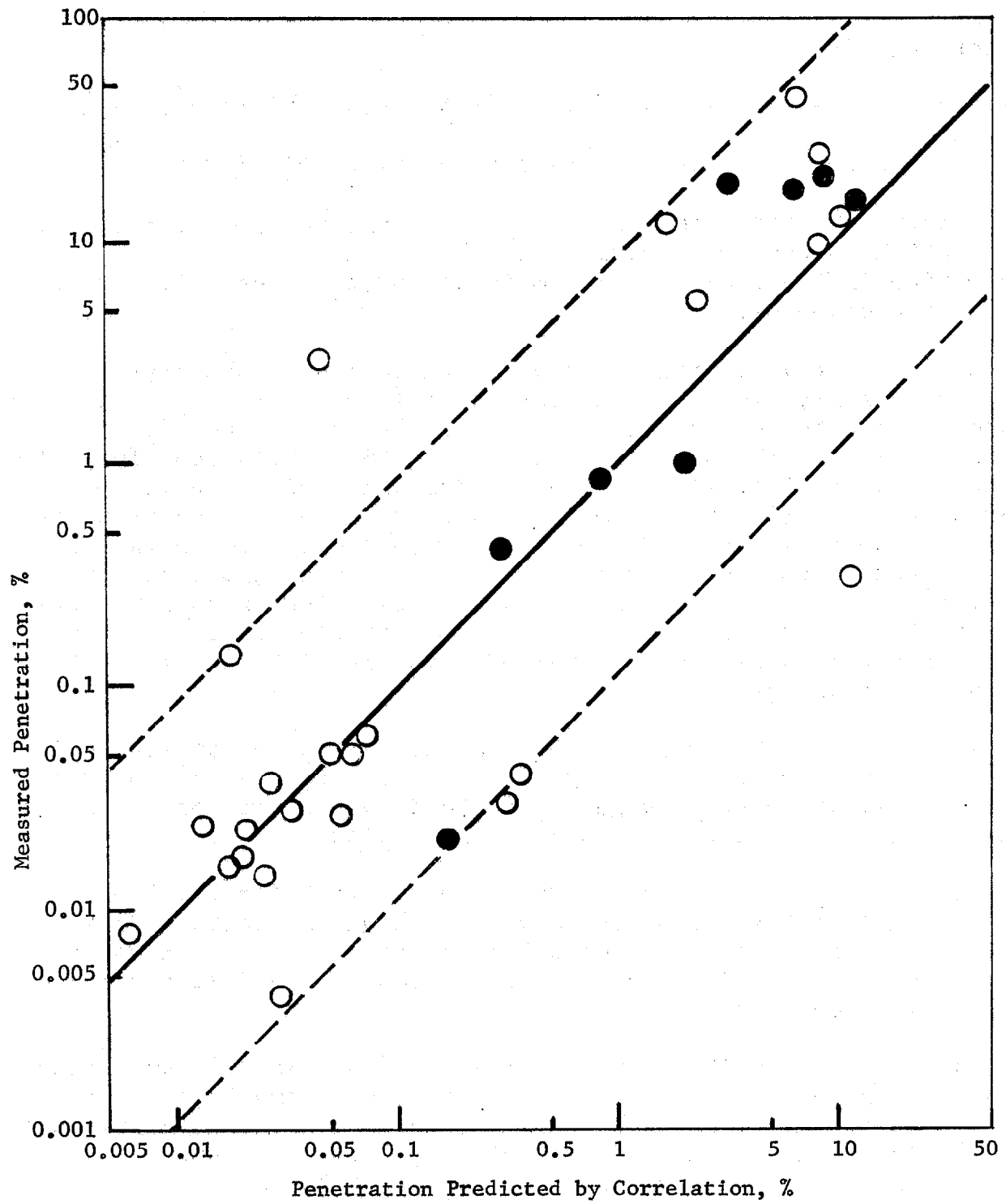
FIGURE 8. CH_3I-131 PENETRATION CORRELATION (AAF TESTS)

Lotting. A lot of adsorber shall consist of a manufacturer's single batch or run of media, made from essentially constant materials by essentially constant manufacturing procedures. If a lot is shipped in multiple drums, these shall contain essentially equal weights of the media, and shall be serially numbered for random-sampling purposes.

Sampling. Samples shall be obtained in either of two ways: by capture from the freely falling stream of media during the drum-filling process, or by means of a grain thief, in accordance with ASTM E300, Sec 26.4.2.2. The minimum number of samples drawn from each lot shall be the weight of the lot in kg, divided by 2500; for especially critical applications, the number of samples drawn shall conform to the tables of MIL-STD-105D, Single Sampling Plan, Standard Requirements, AQL 4.0, with each drum constituting an 'item'. Sample size shall be at least 200 g; these shall be immediately placed in sealed bottles.

Test Canister. The test canister shall be as shown in Figure 6. The length 'A' shall be (equal to the depth of the bed for which the media is to be used) (___ + 2 mm) (50 + 2 mm). The canister shall be filled by free fall, using the apparatus of ASTM D2854. The distance from the bottom of the funnel to the top of the canister shall be 100 + 5 mm.

Test Apparatus. The test apparatus shall include all elements shown in Figure 3. Each sampling canister (3 upstream, 3 downstream) shall be 19 + 1 mm O.D., 25 + 1 mm long, filled with an absorber which has been shown to be at least 98% efficient under the conditions existing at the samplers in the course of the test. Sampling lines (SL) shall be 304 stainless steel, and shall not exceed 50 cm in length, nor 3 mm I.D. The sampler mixture flow shall be 15 + 2 cm^3/sec. All pressure gages, thermocouples and flowmeters shall provide accuracies of better than + 3% of the absolute quantities measured.

Test Cycle. The test cycle shall consist of a pre-conditioning period of at least 120 minutes, a radiocontaminant feed period of 60 + 1 minute, and an elution period of at least 120 minutes. The specified temperature, pressure and humidity condition shall be maintained throughout the entire elution and feed periods, and for at least the final 60 minutes of the pre-conditioning period. During the first part of the pre-conditioning period, the temperature of the system shall be raised to the specified test level before water vapor is added to the flow.

Temperature and Humidity Measurement and Control. The control of system operating temperature and humidity shall maintain the values of absolute temperature (K) and absolute humidity within + 1% in the course of a run. For operating temperatures below 50 C, humi-

dity shall be measured by wet bulb/dry bulb or dew point techniques; above 50 C, humidity shall be measured by weighing condensate gathered in condenser trap SCT.

<u>Test Conditions.</u> The following test condition shall be run on every sample tested: Temperature, 130 ± 5 C; Relative Humidity, $93 \pm 2\%$; Pressure, 380 ± 20 kN/m^2; Canister face velocity, 20 ± 2 cm/s; Contaminant, CH_3I-127 tagged with CH_3I-131; Contaminant Concentration, 17 ± 2 mg/m^3. (Additional tests at other conditions, including tests with I_2-131, may be specified as needed to evaluate the carbon for some particular service condition).

<u>Activity Counting Procedure.</u> Counts shall be made of each of the six sampler canisters following the test cycle. A 75 mm O.D. NaI scintillation crystal with a 25 mm I.D. well 50 mm deep shall be used to count the 0.364 MeV iodine-131 gamma line. The total of upstream counts shall be at least 10,000. The counting technique shall include a determination of background, and the data analysis shall include a calculation of the probable error in both upstream and downstream counts. The sampler canisters shall be inserted in the crystal well with the inlet face of the canister facing the bottom of the well. Counts of all six sampler canisters shall be corrected for decay rate.

<u>Carbon Characterization.</u> The following characteristics of each carbon sample tested shall be provided along with the results of the radioisotope test:
a) Particle size analysis per ASTM D2862-70;
b) Surface area by dynamic BET method on nitrogen;
c) Hardness by MIL-C-13724B, Sect 4.4.4.2;
d) Moisture content as received by ASTM D2867-70;
e) Bulk Density as received by ASTM D2854-70;
f) Impregnant content.

<u>Data Package.</u> The data package delivered to the purchaser shall include all raw data and calculations needed to substantiate the tests performed. Certifications of results as being in excess of specified values will not satisfy this requirement.

<u>Use of Test Canisters to Measure Residual Filter Life</u>

A continuous problem in nuclear systems is the estimation of 'life' remaining in a carbon filter bank. This can be helped by including in each filter bank a set of test canisters arranged to receive the same exposure as the main bank. The canisters are filled from the same carbon lot as the main bank. One of the canister set is removed at each plant shutdown and tested under conditions identical to the original lot quality control test. A plot

of performance versus time allows the remaining life in the bed to be estimated. Figure 9 shows three ways in which test canister may be installed.

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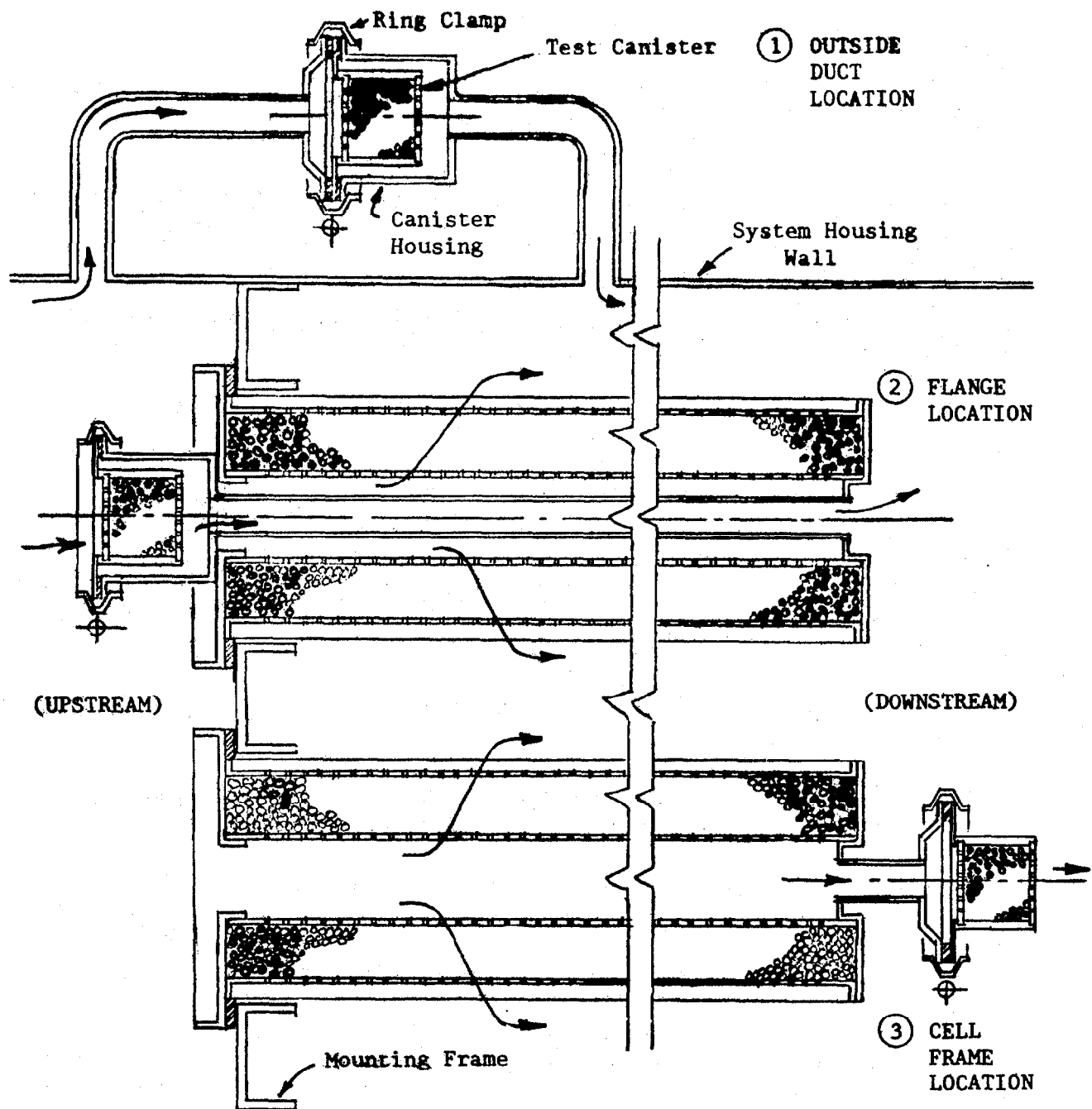
FIGURE 9.   CARBON TEST CANISTER LOCATIONS:'NORMAL' FLOW DIRECTION
(Note: Fittings can be provided to allow gas flow in
opposite direction through filter and test canisters.)

DISCUSSION

BURLEY: I think one comment is in order before we open
the paper for further discussion. The term "standardized test pro-
gram," in this instance, is unique only to a program developed by
Dr. Rivers' company and has no national or international testing
significance. Various test programs and test standards for charcoal
filters are under development by various standards committees but
not one has been issued. To a scientist, it's always appealing
to bring order out of chaos and to see correlation between various
sets of data. I hope we can confine our discussion to the latter
part of the presentation; i.e., to the correlation of test data by
some sort of a unified equation such as is being proposed here.

KOVACH: If I understand correctly the relationship you
showed between your equation and the measured values, you are getting
plus or minus one order of magnitude variation.

RIVERS: That's right.

KOVACH: Do you feel that it is useful at this stage to
use a correlation that gives such a variation in experimental data?
Or is it more important to run tests under the exact conditions that
occur and make sure that the values are obtained under actual use
conditions? Also, you showed filter bank samplers on filters that
have both upflow and downflow sections, though samplers did not
approximate the upflow and the downflow conditions. Do you feel that
testing is reliable on sample units, particularly at high humidities,
when the test conditions do not duplicate the upflow and the downflow
sections of the filter cells?

RIVERS: With regard to whether one should run the tests
for qualification or quality control under any conditions and then
use this correlation to convert to some standard value; certainly
not. This correlation was developed, in part, to enable us to set
quality control limits on the parameters of the carbon itself. One
could not do that until a fairly extensive study had been made of the
effect of such parameters as particle size, surface area, and so
forth, on penetration. We were only partially successful in obtain-
ing a meaninful correlation, but I do feel that for surface area and
for particle size, it has real merit. The effect of impregnation and
concentration of the test contaminant is somewhat dubious.

KOVACH: At very high velocities, say several times
higher velocities than you used to investigate the particle size
effect, there is much less effect between particle size and penetra-
tion. I would like to caution anyone interpreting the results that
they are valid only at very low laminar flow velocities.

RIVERS: There is a very narrow range of velocity data
reported. However, particle size, surface, and concentration of

impregnation vary quite a bit, and the variations were not always intentional. They were simply values for the run-of-the-mill material received, and they taught us that we had to identify these characteristics of the carbon.

As for upflow and downflow, you will notice that some data are starred. These canisters were run upflow; the tests were, however, predominantly downflow. We were not able to note any profound difference between these two situations.

LONG–TERM EFFECTS ON RADIOIODINE TRAPPING BY CHARCOAL* †

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Abstract

The Oak Ridge National Laboratory maintains systems which are designed to provide fission product containment, in the event of accidental release, by continually exhausting air from the containment volume through HEPA filters and charcoal adsorbers. Present practice is to replace charcoal when in-place test results indicate less than 99.9% retention of I_2 for two hours. It is considered possible that a proven capability of trapping $CH_3{}^{131}I$ may be required in the future. A program of tests is underway to determine the $CH_3{}^{131}I$ efficiencies of some commercial impregnated charcoals as a function of time exposed to reactor off–gas. A TEDA-impregnated charcoal retained a high $CH_3{}^{131}I$ trapping efficiency (> 90%) during six months service whereas an iodized charcoal retained that efficiency for only about one month. The $CH_3{}^{131}I$ trapping efficiency test was performed at 90% R.H. with a loading of about 0.4 mg I as CH_3I/cm^3 of bed. This test loading is about ten times larger than the maximum total iodine loading estimated to be possible in ORNL off–gas systems and additional tests are underway to determine whether the trapping efficiencies for a more realistic loading will be maintained for a longer service period.

A second, more urgent problem is related to the slow release of iodine from charcoal beds. The ORNL need is to provide a method of predicting, from a short-term, in-place test result, the fraction of iodine which would be retained over a period of several weeks under accident and post–accident conditions. The results of some long-term (28 day) iodine retention tests are presented and compared with previous results (from ORNL and elsewhere). The releases are larger than acceptable under some conditions. The release depends on at least four environmental parameters: (1) the prevailing relative humidity, (2) the service history, (3) organic contamination in the air and (4) ionizing radiation. Additional tests are in progress to demonstrate the magnitude of the first three of these parameters. It is anticipated that the results of the planned tests, along with those from the Savannah River Laboratory program pertaining to the effects of radiation, will provide an outline of the magnitude of possible iodine releases from adsorbers under ORNL usage. It is suggested that a program of basic studies of the mechanisms involved in iodine trapping and release would help to provide the quality of arguments which may become necessary to defend the efficacy of containment adsorbers.

I. Introduction

The Oak Ridge National Laboratory maintains systems which are designed to provide fission product containment, in the event of accidents, by continually exhausting air from the containment volume through HEPA filters and charcoal adsorbers. Impregnated (in most cases iodized) charcoal is employed and in-place tests (1) of $CH_3^{131}I$ trapping efficiencies are performed. In-place I_2 trapping efficiencies (1) are also periodically measured, and the charcoals are replaced when the in-place I_2 trapping test indicates less than 99.9% retention of I_2 for two hours. The ORNL containment adsorbers are not expected to have to cope with large temperature increases above normal ambient temperature.

It is considered possible that a capability to retain $CH_3^{131}I$ may be required sometime in the future. This would impose two new requirements: (1) a commercially available charcoal which would retain a high $CH_3^{131}I$ trapping capability for a reasonably long period of service and (2) a dependable means for demonstrating, with in-place test data, the efficacy of an adsorber. In an effort to find an adequate, commercially available charcoal which could provide $CH_3^{131}I$ trapping capability for an acceptable service time, we have a program in progress with the objective of demonstrating the relative $CH_3^{131}I$ trapping efficiencies of a TEDA (triethylenediamine) impregnated charcoal and an iodized charcoal as a function of time in reactor off-gas service. Some data from the program are presented.

Another and more urgent problem arises because of the failure of some charcoals, under certain conditions and service history, to retain iodine (I_2) with high efficiency for several weeks (i.e., for the several ^{131}I-half-lives that might be required). We need to understand enough about the processes of long-term iodine release from charcoal to predict the long-term retention efficiency from reasonably short-term in-place observations. We have a program of tests in progress which have the objective of demonstrating the magnitude of the effects of various conditions (such as relative humidity, hydrocarbon contamination in the sweep gas, hydrocarbon contamination on the charcoal, and service time) on the iodine release over a 28-day period after iodine loading. Some data from this program are also presented.

II. Poisoning of $CH_3^{131}I$ Trapping Capability

A. Procedure

A series of samples of TEDA-impregnated and of iodized charcoal were exposed to reactor off-gas air streams. Samples were removed at two-month intervals; the $CH_3^{131}I$ trapping efficiencies and B.E.T. surface areas were measured.

A series of samples of NAC-G618 (which is a TEDA-impregnated, coconut charcoal prepared by the North American Carbon Company) and a series of samples of NAC-G617 (which is an iodized, coconut charcoal also prepared by the North American Carbon Company) were exposed to LITR-BSR off-gas (air) beginning in April 1970. A series of samples of the NAC-G617 charcoal were also exposed to HFIR off-gas during the same time period.

Each sample was contained in a test-bed holder of the kind shown in Fig. 1; these holders were sections of 1-in. diameter glass pipe which retained, with a system of screens and bands, two 1-1/8-in. deep beds of the charcoal to be tested. Two batteries of charcoal test-beds were mounted on separate racks with an appropriate system of valves and piping. One battery of test-beds was installed so
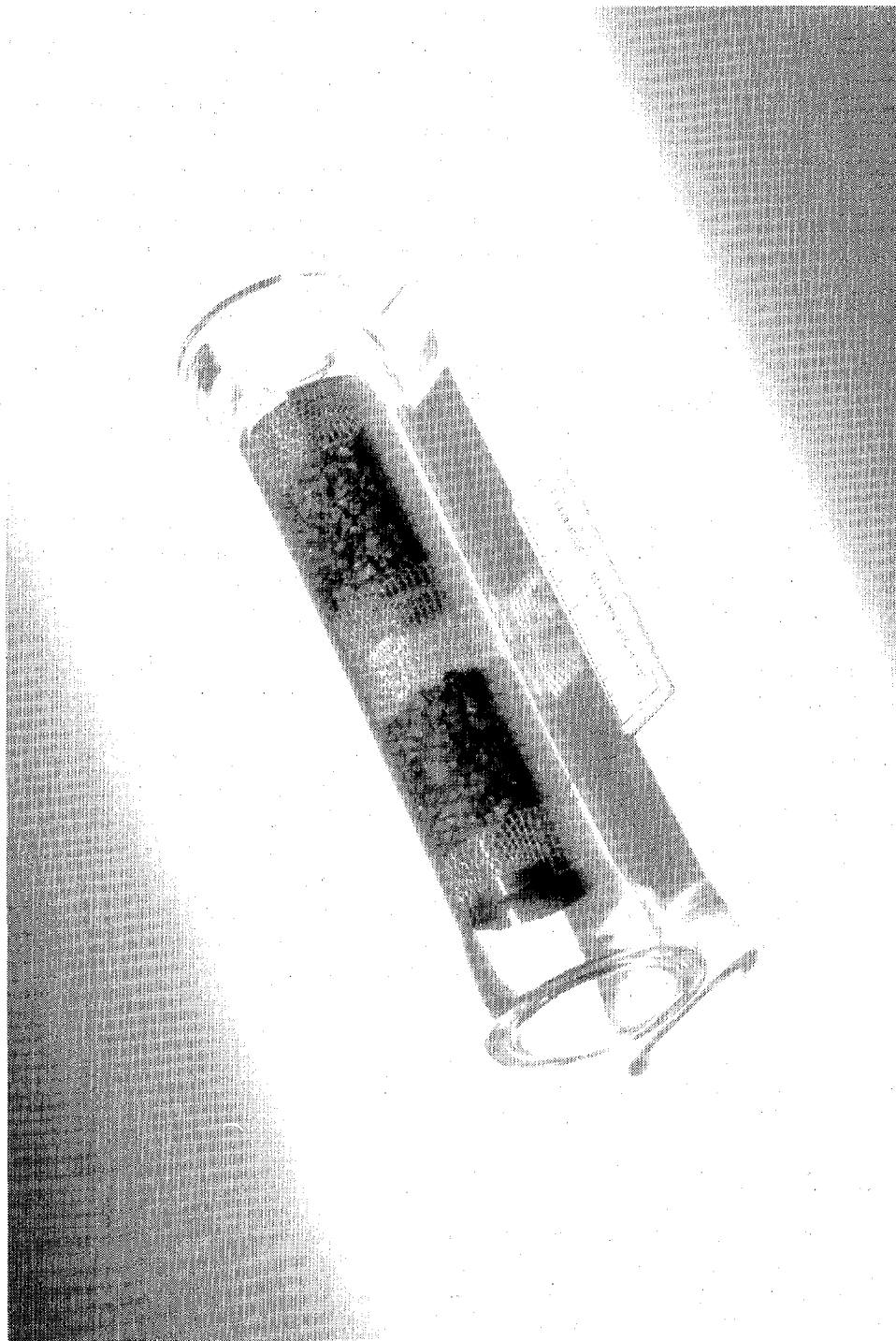
Figure 1. Adsorber Test–Bed Holder.

as to expose the charcoal to off-gas sampled upstream of the LITR-BSR containment adsorber and the other was similarly installed relative to the HFIR containment adsorber. The air velocity through each test-bed was controlled with a separate valve to a value of 40 fpm.

The LITR-BSR ventilation system exhausts air from both the BSR (the Bulk Shielding Facility which is a swimming pool type of reactor) and the LITR (the old Low Intensity Test Reactor which is no longer operating). The air from the LITR is added for humidity control. The LITR-BSR ventilation system contains a long metal duct, upstream of the charcoal adsorbers, which is exposed to the weather; consequently, this off-gas stream undergoes large daily fluctuations in temperature and relative humidity. Figure 2 shows the daily maximum and minimum values of temperature and relative humidity during the period of exposure. Generally the range of the daily temperature variation was about 20°F. The range of the daily relative humidity variation was larger during the first two months than it was later; it commonly varied within a 35-65% R.H. range.

The HFIR (High Flux Isotopes Reactor) off-gas system exhausts conditioned air through a filter-adsorber system which is reasonably well insulated from the weather. The temperature and humidity do not, therefore, undergo very large daily oscillations.

A set of test-beds was removed from the exposure systems at two-month intervals. The specific days at which test-beds were removed are indicated on Fig. 2. The test-beds were installed in a laboratory-test system without disturbing the charcoal and the efficiency for trapping $CH_3{}^{131}I$ was measured.

The laboratory-test system consists of a gas train in which the temperature and relative humidity of the air stream is adjusted (to 25°C and 90% R.H.), and then passed through the test-bed at 40 fpm, and finally through a series of collection beds of charcoal. After passing the conditioned air through the gas train for a period of time to allow equilibration of the charcoal to the test relative humidity, an amount of $CH_3{}^{131}I$ (corresponding to 0.4 mg of I as CH_3I per cm^3 of charcoal bed) was injected. The air stream was continued for an afterpurge period. Finally, the relative count rates for the ^{131}I on each of the two 1-1/8-in. test bed sections and the collection beds were determined and the fraction of the ^{131}I retained on the first 1-1/8-in. test-bed section and on the whole 2-1/4-in. test bed was calculated. Values of experimental conditions are listed in Table 1.

After the $CH_3{}^{131}I$ trapping test, the first of the two 1-1/8-in. test bed sections was removed from the samplers and mixed. The B.E.T. surface area was measured on a portion of this mixed sample.

B.   Results and Discussion

The B.E.T. surface area values are plotted on Fig. 3 as a function of service time for each combination of charcoal and exposure conditions. The decreases in surface area with time in service on the LITR-BSR off-gas system were about the same for the TEDA-treated and the iodized charcoals. The loss of surface area by the iodized charcoal was less during service on the HFIR system than on the LITR-BSR system. The temperature and humidity fluctuations in the LITR-BSR off-gas may be responsible for the more rapid decrease in surface area. The rate of loss in surface area for the samples exposed to the HFIR off-gas was similar in magnitude to that observed by Evans(2) in unimpregnated charcoals after exposure to Savannah River Reactor off-gas (air).
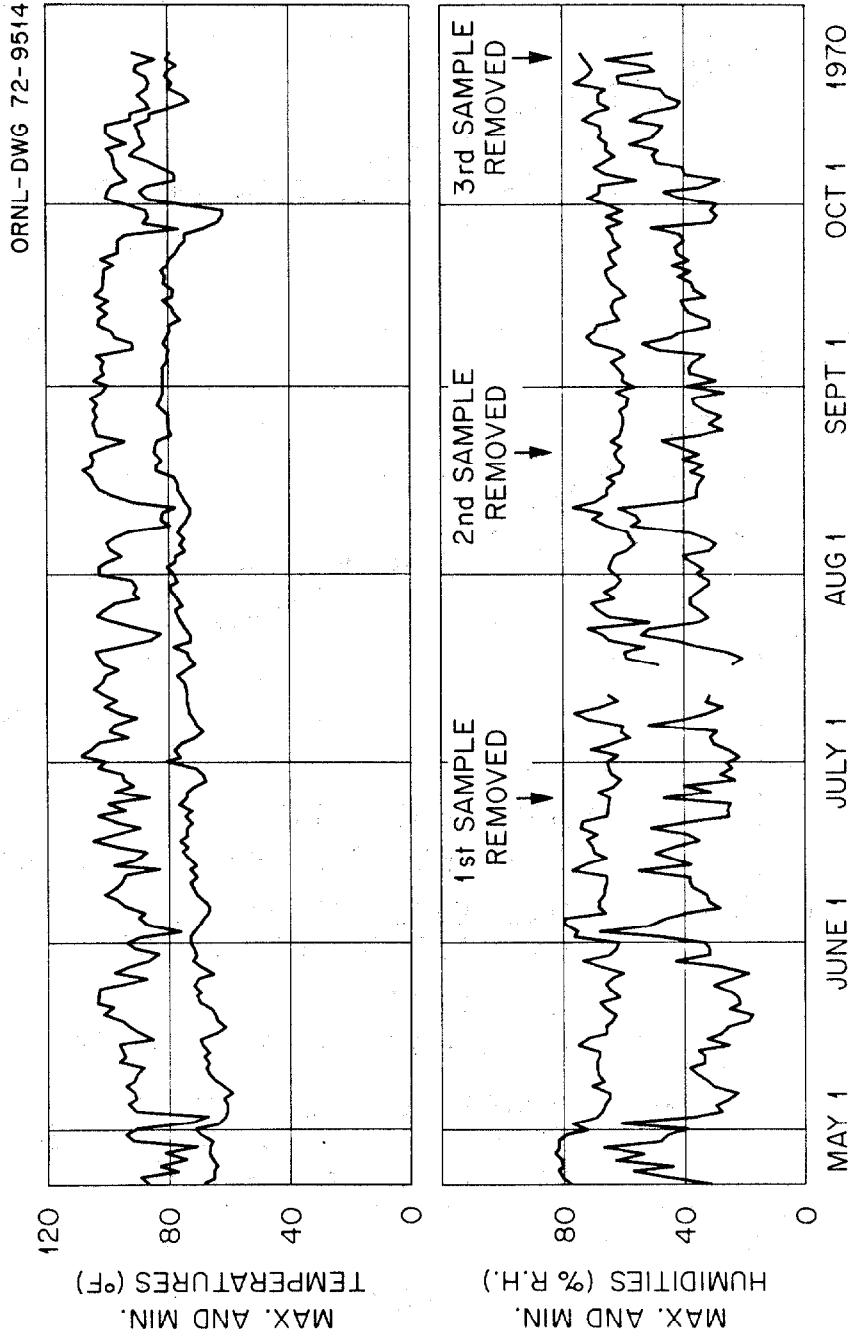
ORNL-DWG 72-9514

Figure 2. Maximum and Minimum Temperatures and Relative Humidities of the Off-Gas at the
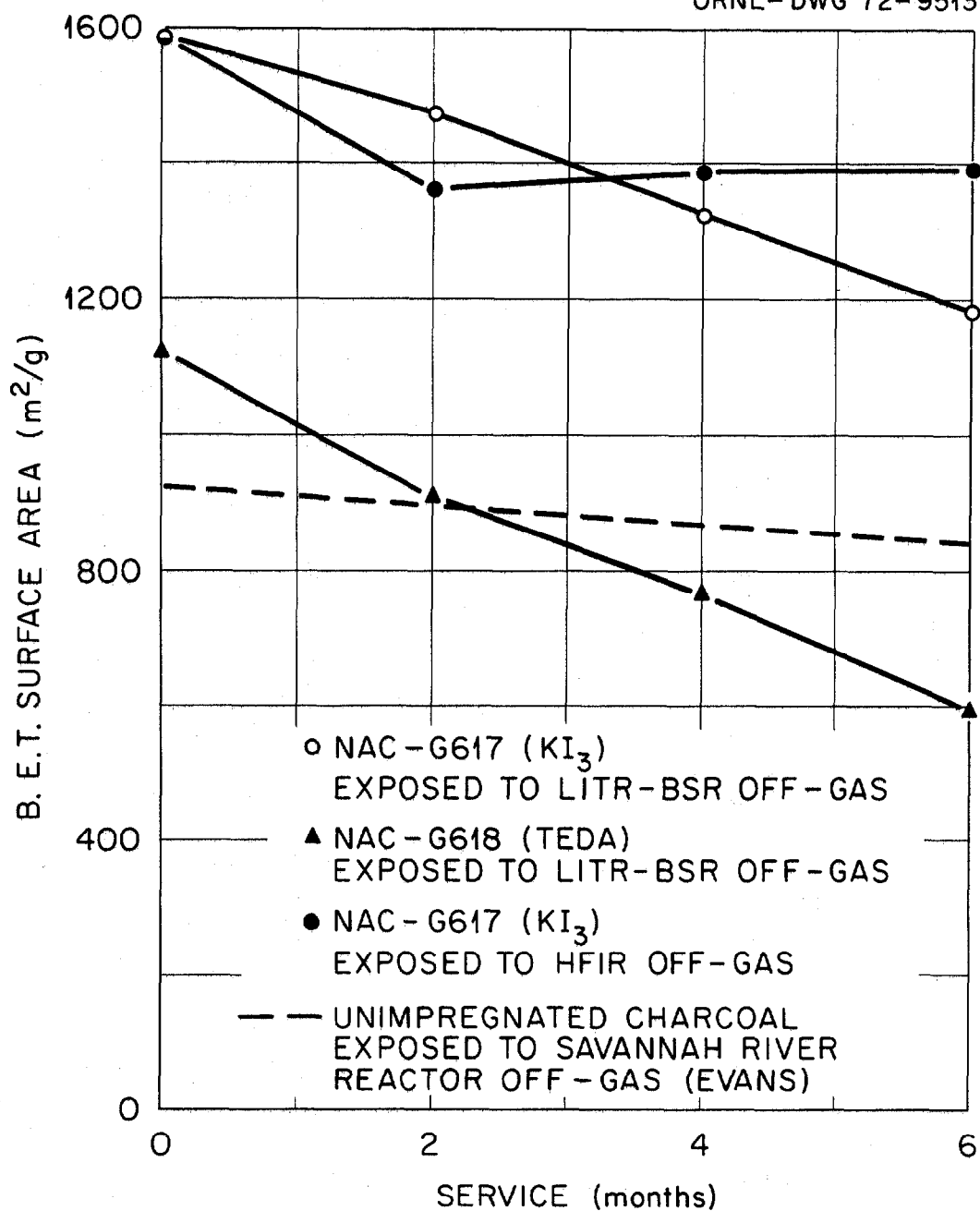LITR-BSR Filter-Adsorber System.

ORNL–DWG 72–9513

Figure 3. Reduction in B.E.T. Surface Area with Service Time.

Table 1. Conditions for Methyl Iodide Decontamination Tests on LITR – BSR– and HFIR-Exposed Samples

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Each test bed section: Two 1-1/8-in. deep beds in series, 1-in. bed diam.

Each collection bed section: four 1-in. deep beds of MSA 85851, 8 x 16 mesh (U.S.), in series; 1-in. bed diam.

Methyl Iodide Test Conditions:

Temperature, pressure: approximately 25°C, 1 atm

Air face velocity: 40 fpm

Superficial residence time for each 1-1/8-in. depth: 0.14 sec

Relative humidity: 90%

Preequilibration time: around 18 hr

Methyl iodide injection time: 2 hr

Afterpurge time: 4 hr

Inlet CH_3I concentration: around 17 mg/m^3

Weight I as CH_3I injected per volume of charcoal in 2-1/4-in. depth: around 0. 4 mg/cm^3

The $CH_3{}^{131}I$ fractional penetrations are shown in Fig. 4 as a function of bed depth and service time for three combinations of charcoal and service. The zero exposure data, in each case, show the commonly observed linearity between the logarithm of the fractional penetration and bed depth.(3) This relationship can be predicted with a homogeneous bed. After a period of time in service, the linear relation fails; the logarithm of the fractional penetration through the first half of the bed is relatively higher than that through the second half. This is consistent with the postulate that the loss of $CH_3{}^{131}I$ trapping capability is due to poisoning by contaminants in the air; the front half of the bed removes some of the contaminants and partially protects the back half of the bed.

A major practical point is that a considerable loss of $CH_3{}^{131}I$ trapping efficiency (or increase in fractional penetration values) was observed in all three cases after only six-months service. The iodized charcoal (NAC-G617) showed a small difference in rate of poisoning at the two off-gas systems. The LITR-BSR off-gas (which undergoes large daily temperature and relative humidity fluctuations) resulted in somewhat faster loss of $CH_3{}^{131}I$ trapping capability.

A comparison of the results for the iodized charcoal (NAC-G617) with those for the TEDA-impregnated charcoal (NAC-G618), both exposed to the same gas stream, reveals that the TEDA-treated material retained a trapping efficiency in excess of a given value for a longer service time than did the iodized charcoal. For instance, the TEDA material retained a $CH_3{}^{131}I$ trapping efficiency greater than 90% for six months service, whereas the iodized charcoal retained that efficiency for about one month.
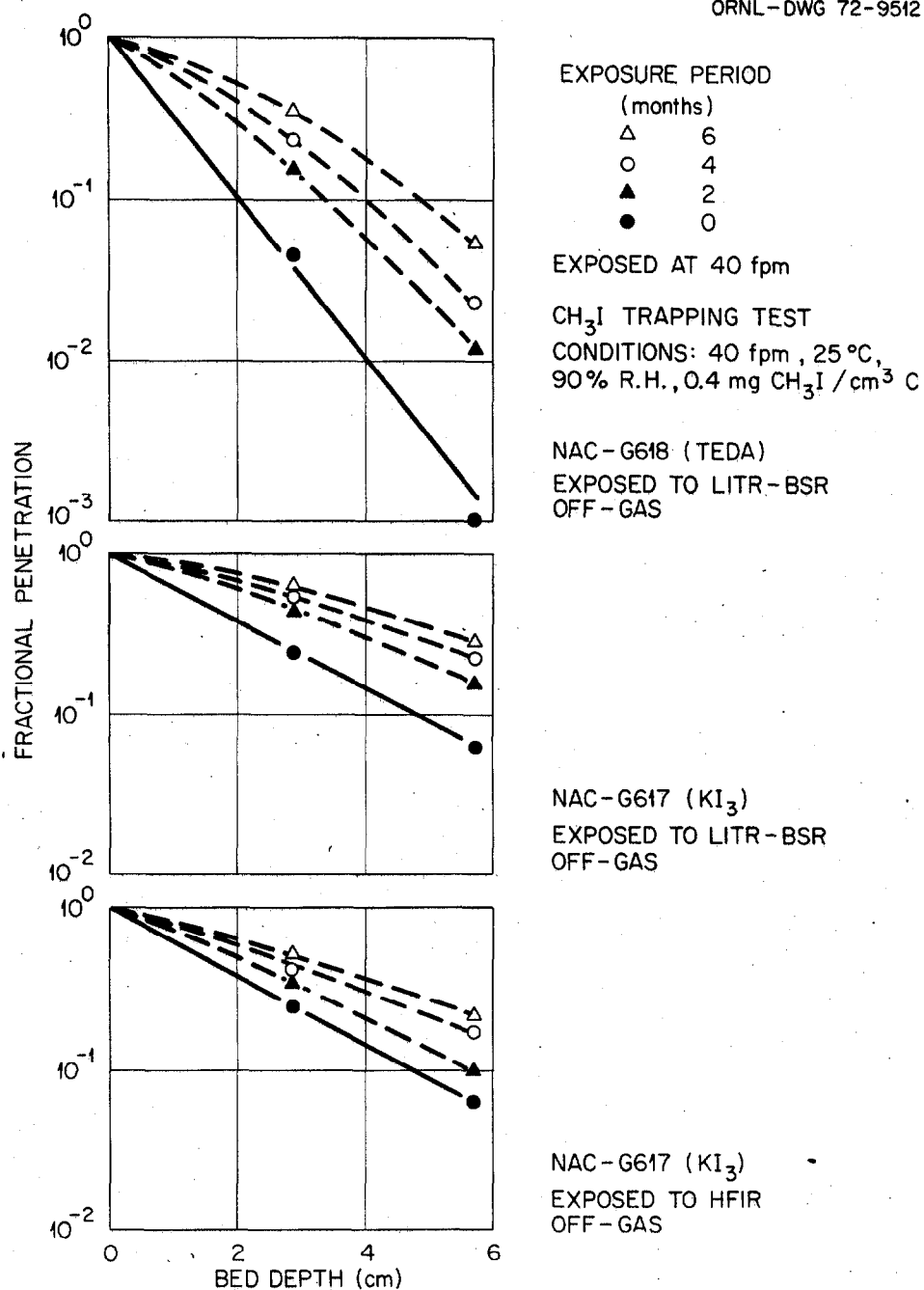
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EXPOSURE PERIOD
(months)

△	6
○	4
▲	2
●	0

EXPOSED AT 40 fpm

CH_3I TRAPPING TEST
CONDITIONS: 40 fpm, 25 °C,
90% R.H., 0.4 mg CH_3I /cm^3 C

NAC-G618 (TEDA)
EXPOSED TO LITR-BSR
OFF-GAS

NAC-G617 (KI_3)
EXPOSED TO LITR-BSR
OFF-GAS

NAC-G617 (KI_3)
EXPOSED TO HFIR
OFF-GAS

FRACTIONAL PENETRATION

BED DEPTH (cm)

Figure 4. Poisoning of $CH_3{}^{131}I$ Trapping Capability.

The $CH_3{}^{131}I$ trapping test conditions are not considered to be excessively conservative in comparison to accident conditions except in regard to the loading. The maximum accident iodine loading for some ORNL off-gas system adsorbers is about 3×10^{-2} mg/cm^3 which is about an order of magnitude less than the CH_3I loading employed. Further tests are in progress to determine rates of poisoning on the basis of $CH_3{}^{131}I$ trapping tests made at lower loadings.

There is a qualitative correlation between the effects of exposure conditions (i.e., LITR-BSR off-gas vs HFIR off-gas) on the rate of loss of B.E.T. surface area and on the rate of loss of $CH_3{}^{131}I$ trapping efficiency. Without more basic descriptions of the $CH_3{}^{131}I$ trapping mechanisms than are available one can only speculate as to the possible significance and/or usefulness of this correlation.

III. Release of Iodine from Charcoal Beds

A. Procedure

These tests are being done on a laboratory gas train system having three test bed sections in parallel. In this system the air stream was first adjusted to the desired temperature (27°C) and relative humidity. The air was passed through the 2-in. (or in some cases, 1-1/8 or 2-1/4-in.) deep, 1-in. diameter test beds of charcoal followed by a series of charcoal collection beds. The controlled air was first passed through the train for about 22 hours to allow equilibration of the charcoal with the air. An amount of ^{131}I-labeled I_2 was put into the gas stream and air continued to pass through the system (at 40 fpm). At intervals of time during a 28-day period, the collection beds were replaced. Counting of the test bed and collection beds provided the information from which was calculated the fraction of iodine retained after each interval of time. In most of the tests, one branch of the gas train contained a test bed section of unimpregnated charcoal (BC-416), the second branch contained a test bed section of iodized charcoal (Witco-42) and the third branch contained a test bed section of TEDA-impregnated charcoal (NAC-G618).

In the tests done thus far, the relative humidity was 0% R.H. in one experiment and 90% R.H. in another. In a third test, at 90% R.H., the vapors from a mixture of hydrocarbons (benzene, toluene, cyclohexane and heptane) were included, at a concentration of 0.0018 volume percent, in the purge air starting immediately after the I_2 was loaded into the bed. The hydrocarbons were added to simulate impure ambient air.

B. Results from This Study and Comparison with the Results of Others

The results are presented in Figs. 5, 6, and 7 along with previously reported results which also pertain to iodine release from charcoal beds at room temperature.

Figure 5 is a presentation of data pertaining to release of iodine from unimpregnated charcoals. The results from this study show that the release from new, unimpregnated charcoals was greater into air of 90% R.H. than into air of 0% R.H. Only a slight further increase was observed for release into 90% R.H. air containing hydrocarbon vapor at a concentration of 0.0018 volume percent. In all three cases the releases were small; they were less than 10^{-4} of the total loading.

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	RESEARCHER	DESIGNATION	MESH (U.S.)	BASE	R.H. (%)	DEPTH (in.)	VELOCITY (ft/min)	LOADING (mg/cm³)	REMARKS
□	THIS STUDY	BC-416	8 x 16	COCONUT	0	2	40	4×10^{-2}	
○	CARON *et al.*	TS	~ 8 x 16	COAL	15	2	60	0.2	CONTINUOUS LOADING
■	THIS STUDY	BC-416	8 x 16	COCONUT	90	2	40	4×10^{-2}	
●	CARON *et al.*	TS	~ 8 x 16	COAL	90	2	60	0.2	CONTINUOUS LOADING
△	EVANS *et al.*	—	8 x 16	COCONUT	10	1	68	2	1.5×10^{7} r/hr γ-FIELD
▽	EVANS *et al.*	—	8 x 16	COCONUT	10	1	68	2	36 mos, SERVICE, γ-FIELD
▲	THIS STUDY	BC-416	8 x 16	COCONUT	90	2	40	4×10^{-2}	0.0018 % HC's IN SWEEP GAS
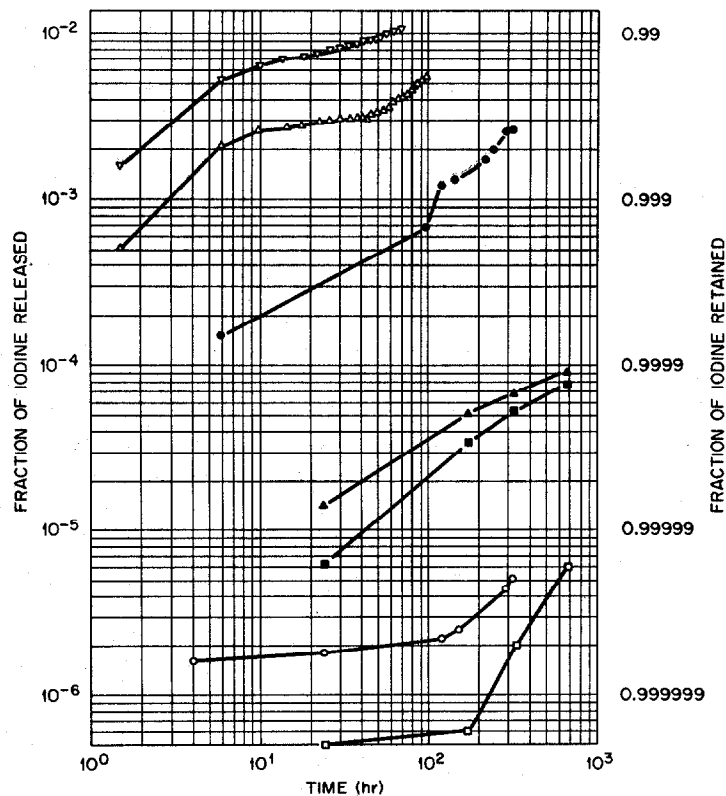
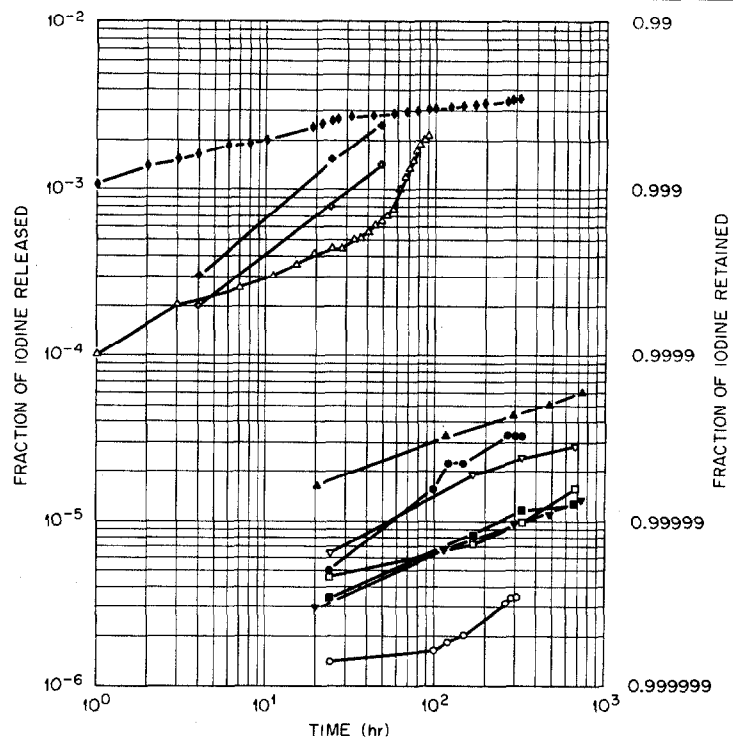Figure 5.   Iodine Release from Unimpregnated Charcoal.

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Figure 6. Iodine Release from Iodized Charcoal.

ORNL-DWG 72-9509

RESEARCHER	DESIGNATION	MESH (U.S.)	BASE	R.H. (%)	DEPTH (in.)	VELOCITY (ft/min)	LOADING (mg/cm^3)	REMARKS
THIS STUDY	NAC-G618	8×16	COCONUT	0	2	40	4×10^{-2}	
THIS STUDY	NAC-G618	8×16	COCONUT	90	2	40	4×10^{-2}	
THIS STUDY	NAC-G618	8×16	COCONUT	90	1⅛	40	0.2	
THIS STUDY	NAC-G618	8×16	COCONUT	90	2	40	4×10^{-2}	0.0018 % HC's IN SWEEP GAS

□ ■ ◄ ►
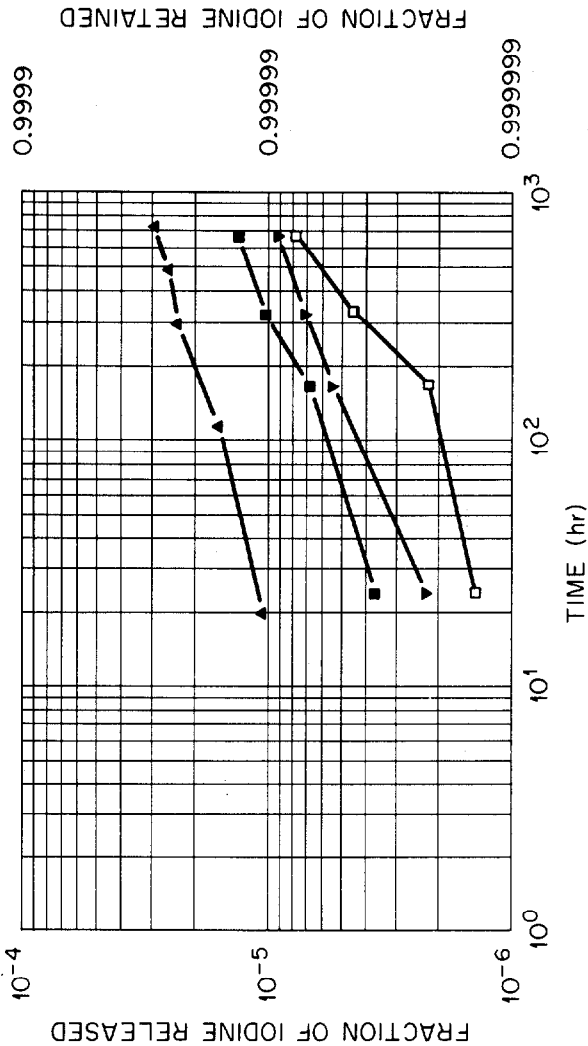

Figure 7. Iodine Release from TEDA-Impregnated Charcoal.

Caron et al.(4) did a series of experiments in which charcoal beds were exposed continuously for about two weeks to an air stream containing 1 mg I_2/m^3. Under these conditions, low release values were observed at low (15%) relative humidity but quite high release values were observed into 90% R.H. air. This observation may have resulted from some fraction of the iodine being in the form of organic iodides, since there is an apparent tendency in experimental systems for a significant fraction of iodine at low concentration to become organic iodide (3).

The results of Evans et al. (5) are also plotted on Fig. 5. They show the relatively large releases which were observed from a bed of new charcoal while exposed to a 1.5×10^7 rad/hr Co-60 gamma field and the even larger releases observed from a bed of charcoal which had seen three years service prior to the test of release during exposure to the gamma field.

The results from this study with iodized charcoal are shown on Fig. 6, along with results from other studies. In this study, one test with an iodized charcoal prepared from petroleum coke (Witco-42) showed very low release into 0% R.H. air. Two tests of the same charcoal showed almost the same release into 90% R.H. air. One test with a shallower bed (namely 1-1/8-in. as compared to the 2 or 2-1/4-in. beds in the previously mentioned tests) on iodized coconut charcoal (NAC-G617) also resulted in low releases (i.e., $< 10^{-4}$ of the total). One test in which a bed of iodized petroleum coke charcoal (Witco-42) was subjected to 90% R.H. air containing 0.0018 volume percent of hydrocarbon resulted in a significant increase in the release but the release was still quite low (i.e., well below 10^{-4} of the total).

For comparison, results from Caron et al. (4), who did tests in which the test beds were continuously exposed to a low concentration of I_2 for a long time, are also plotted on Fig. 6. At both low and high relative humidity, Caron et al. observed low releases which compare well with the observations from the present study.

Adams et al. (6) subjected an iodized, coconut charcoal (BC-727), after loading with iodine, to a gas stream containing quite high concentrations of hydrocarbons. In one experiment the gas stream contained about 0.07 volume percent diethylbenzene; in the other experiment Amsco 125-82 vapor at a concentration which was probably of the same order of magnitude was employed. The concentrations corresponded to an estimated 40% saturation. These experiments resulted in high releases, well over 10^{-3} of the total loading in 48 hours.

Pope and Smith (7) experimented with a 2 ft x 2 ft, pleated bed adsorber module which contained iodized coconut (BC-727) charcoal and which had been in service for about a year. They loaded the bed with a quantity of iodine and then swept it with ambient air. As can be seen by reference to Fig. 6, 10^{-3} of the loading was released in an hour and about 3.5×10^{-3} of the loading was released in two weeks.

A result from the experiments of Evans et al. (5) of iodine release from an iodized coconut charcoal bed while exposed to a 1.5×10^7 rad/hr Co-60 gamma field is also plotted. The observed release in this experiment was high; it exceeded 10^{-3} of the total loading in a few days.

Figure 7 is a presentation of the results from the present study with TEDA-impregnated, coconut charcoal. The results show an increase in the release into 90% R.H. air over that observed in 0% R.H. air. The release observed into the 90% R.H. air containing 0.0018 volume percent hydrocarbons was slightly less than that observed with 90% R.H. air without hydrocarbons. The difference may not be significant.

C. Discussion

Our ultimate objective is to provide a defendable way to predict, from an in-place measurement of the release into ambient air during a several hour period, the release that could occur over a period of several weeks under accident conditions. It seems to be clear from a survey of the results on Figs. 5 and 6 that accident releases could be greater than 10^{-3} of the total loading from a charcoal bed which had been indicated by an in-place test to release less than 10^{-3} of the total in two hours. (The 10^{-3} value is the allowable fractional release from ORNL containment adsorbers.) It appears that the release depends on at least four environmental parameters: (1) the relative humidity, (2) the service history, (3) organic contamination in the air and (4) ionizing radiation. The experiments, which we have in progress, have the objective of demonstrating the magnitude of the effects of the first three of these parameters. It is anticipated that the results of these experiments along with those from the Savannah River Laboratory program pertaining to the effects of radiation (5,8), will provide an outline of the magnitude of possible iodine releases from charcoal adsorbers under ORNL usage.

It is suggested that an effort toward a more basic understanding of iodine trapping on adsorbers or by other means should be in progress. Although the testing of commercial products under specific conditions anticipated in use is obviously necessary, a better understanding of the processes involved may also become necessary to the development of arguments to adequately defend the efficacy of containment adsorbers.

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EFFECT OF EXTENDED EXPOSURE TO SIMULATED LMFBR FUEL REPROCESSING OFF-GAS ON
RADIOIODINE TRAPPING PERFORMANCE OF SORBENTS* †

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Abstract

For LMFBR fuel reprocessing plants, a required radioiodine retention factor of $\sim 10^8$ is projected. Also projected is a cumulative retention factor of $\sim 10^6$ for iodine fixation achieved upstream of the filter-adsorber assembly used for final off-gas treatment. Thus, this assembly will need to provide a decontamination factor (DF) of $\sim 10^2$, but considerable reserve capability is desired. Certain silver-containing sorbents in a 2-in. depth at 100°C and/or 200°C have, in short-term laboratory tests, exhibited DF's of $> 10^3$ for iodine as methyl iodide or elemental iodine under conditions including 3 vol % water vapor and iodine loadings estimated equivalent to that for at least one year of operation. Present objectives are to obtain information on the effective service life of such sorbents and to ascertain the desirability of locating a catalytic oxidation bed upstream of the sorbents to minimize poisoning by organics and to convert organic iodides to I_2. Accordingly, a laboratory facility for exposing sorbents to simulated fuel reprocessing off-gas is being operated. The main air stream is humidified to around 85% saturation (referred to room temperature). Elemental iodine (60-day ^{125}I-labeled), dodecane, and nitric oxide are continuously injected at their anticipated concentrations. One group of sorbents is exposed to untreated off-gas while another group is exposed to off-gas which has traversed a Hopcalite bed at 350°C. Methyl iodide (12.3-hr ^{130}I-labeled) is injected periodically to furnish short-term results, whereas long-term cumulative results are obtained with the I_2.

Sorbents investigated include three varieties of silver zeolite (designated AgX with the percent Ag^+ for Na^+ exchange denoted), GX135 (silver salt-treated alumina-silica), and a type of iodized charcoal. Sorbent depths are 2 in. Excellent performance (indicated I_2 and CH_3I DF's $\geq 10^3$) has been observed thus far for the following test situations: 26% AgX, 1/16-in. pellets, at 200°C, both with and without Hopcalite upstream, 196 days exposure; 99% AgX, 1/16-in. pellets, 100°C, both with and without Hopcalite, 105 days; GX135 (8 x 16 mesh, U.S.), 200°C, with Hopcalite, 196 days; and GX135, 100°C, without Hopcalite, 119 days. (Data are not yet available for GX135, 100°C, with Hopcalite.) Performances observed for other test situations ranged from poor to good. The importance of sorbent particle size was demonstrated by the less favorable performance of 88% AgX, 1/8-in. pellets, 100 and 200°C, relative to that for the 26% AgX, 1/16-in. pellets (200°C). The use of Hopcalite was observed highly beneficial in trapping iodine injected as CH_3I; in trapping iodine injected as I_2, its use was beneficial for 26% AgX, 99% AgX, and GX135 and deleterious for 88% AgX (1/8-in. pellets) and iodized charcoal (the latter at 66°C). This investigation is being continued.

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†This paper and the preceding one entitled "Long-Term Effects on Radio-iodine Trapping by Charcoal" were presented orally by the same authors as a single paper entitled "Long-Term Effects on I_2 and Ch_3I Trapping."

I. Introduction

In LMFBR fuel reprocessing plants, radioiodine control will be a major problem since rather large amounts of short-cooled fuel are to be involved. For an appropriately-sized plant, a required radioiodine retention factor of $\sim 10^8$ (over-all) is projected. Also projected is a cumulative retention factor of $\sim 10^6$ corresponding to iodine removal achieved upstream of the final off-gas trapping system. The latter value is based on consideration of iodine fixation resulting from mechanisms inherent in the fuel reprocessing operations and on evaluation of the expected performance of iodine removal equipment (exclusive of the final trapping system) incorporated in the reprocessing facility. Accordingly, the filter-adsorber assembly employed for final treatment of the off-gas will need to provide a radioiodine decontamination factor (DF) of $\sim 10^2$, but considerable reserve capability would, of course, be desirable. The overall problem of iodine retention in LMFBR fuel reprocessing plants, as outlined above, has been discussed in considerably greater detail by Yarbro, Crouse, and Cathers.(1) The Chemical Technology Division at ORNL is conducting a rather extensive investigative program on this iodine retention problem as a part of their larger program on LMFBR fuel reprocessing.(2) The work described herein represents a part of the program relating to iodine retention and, more specifically, is concerned with determining the applicability of various sorbents for trapping iodine in the off-gas assembly employed for final treatment.

Certain silver-containing sorbents in a 2-in. depth at 100°C and/or 200°C have, in short-term laboratory tests, exhibited DF's of $> 10^3$ for iodine either as methyl iodide or as elemental iodine under conditions including 3 vol % water vapor and iodine loadings at least equivalent to that estimated for one year of operation (~ 5 mg iodine per cm^3 sorbent in 2-in. depth).(3) Two of these effective sorbents were laboratory-prepared and are referred to as silver zeolites (or, alternately, silver-sodium zeolites) with the degrees of Ag^+ for Na^+ exchange having been approximately 27% and 90%. The selection of these sorbents for investigation in connection with treating LMFBR fuel reprocessing off-gas was, of course, prompted by the development reported by Maeck, Pence, and Keller (4), viz., that silver zeolite is highly effective for trapping iodine in the forms of methyl iodide and elemental iodine. (They mentioned the possible potential of silver zeolite for removing iodine from fuel reprocessing off-gas.) Another effective material was a silver-containing inorganic sorbent obtained from a commercial source (GX-135).

While silver-containing sorbents are expensive, the quantity of off-gas to be treated is estimated to be relatively small (~ 500 cfm for a typical plant); therefore, extremely large quantities of a highly effective sorbent would not be required.

Present objectives are to obtain information on the effective service life of these promising sorbents and to ascertain the desirability of locating a catalytic oxidation bed upstream of the sorbents. The oxidation bed has two functions: (1) to minimize poisoning by destroying organics which might be adsorbed and (2) to convert organic iodides to elemental iodine and thus improve trapping efficiency.

II. Experimental

In this continuing investigation, selected sorbents are exposed to simulated LMFBR fuel reprocessing off-gas for extended periods of time which have varied, for different sorbent-condition combinations, from 77 days to beyond 196 days. One group of sorbents is exposed to untreated off-gas, while another group is exposed

to off-gas which has traversed a catalytic oxidation bed. Periodically, trapping data for iodine injected as elemental iodine and as methyl iodide are obtained. The experimental modes are such that the results for elemental iodine are basically long-term, while those for methyl iodide are short-term.

Apparatus and Operating Conditions

A schematic diagram of the laboratory facility that is employed is shown in Fig. 1. In its construction, stainless steel type 316 was employed almost exclusively where corrosion might present a problem. Not shown are the various flow meters which are utilized, including the ten exit flowmeters. Dimensions of the sorbent beds and the catalytic oxidation bed (Hopcalite) are given in Table 1 together with certain of the operating conditions such as off-gas velocities and target concentrations for the additives. The reported temperatures are based on readings exhibited by thermocouples with junctions located, in each case, on the centerline immediately downstream of the sorbent or catalyst and, considering the gradients present, are regarded as being representative of the mean values.

During operation of the facility, the main air stream is humidified to the extent of around 85% saturation referred to room temperature (near 26°C). Dodecane* and nitric oxide** are introduced continually into the main air stream to provide concentrations which, on the basis of long term usage, do not differ from the target concentrations by more than about 30%. Elemental iodine, labeled with ^{125}I (60-day half-life), is also continuously injected except for relatively brief periods when the supply is exhausted or some similar reason pertains. (On occasion, operation of the facility is suspended, e.g., to change out the Hopcalite.) While different batches of I_2 were injected during the 196 days of operation covered herein, they were all prepared so as to have nearly the same specific activity at any particular time. As indicated in Table 1, the iodine concentrations of principal interest are those pertaining to the off-gas as it enters the sorbent beds; the concentrations quoted were evaluated using the amounts of ^{125}I found on removed sorbent beds and their associated collection beds. This approach was employed as a consequence of the uncertain amount of iodine deposition in the injection line, connecting lines, etc.

While elemental iodine is injected on a generally continuous basis, methyl iodide, ^{130}I-labeled (12.3-hr half-life), is injected only periodically (roughly bimonthly) and then essentially as a pulse. The injection is probably complete in about 3 min.

Oxidizing Catalyst and Sorbents

Such materials as were initially installed and indicated by letters in Fig. 1 follow:

H   Hopcalite, MSA Part No. 21215, 8 x 16 mesh (U.S.), from Mine Safety Appliances Company. Its use as related to the iodine trapping problem has been investigated.(5, 6, 7, 8)

A   Activated carbon, iodized, Grade 42, 8 x 16 mesh (U.S.), from Witco Chemical Corporation.

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*   Practical, MP - 10.5 to - 9°C, from Matheson Coleman and Bell.
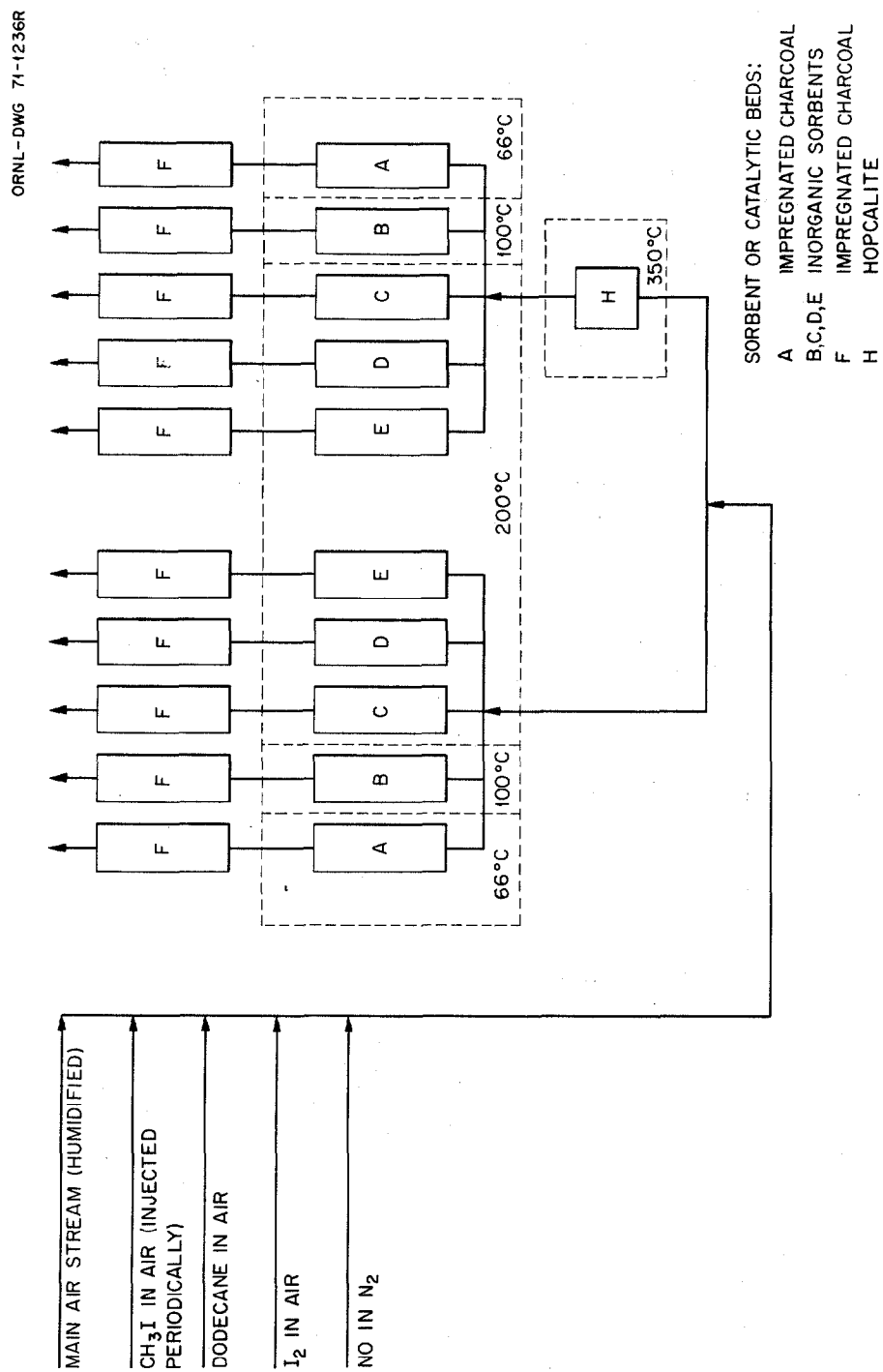
** Technical grade, from the Matheson Company, Inc.

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MAIN AIR STREAM (HUMIDIFIED)

CH$_3$I IN AIR (INJECTED PERIODICALLY)

DODECANE IN AIR

I$_2$ IN AIR

NO IN N$_2$

SORBENT OR CATALYTIC BEDS:

A	IMPREGNATED CHARCOAL
B,C,D,E	INORGANIC SORBENTS
F	IMPREGNATED CHARCOAL
H	HOPCALITE

Figure 1. Flow Diagram of Apparatus for Investigating Effects of Long—Term Exposure to Simulated Off—Gas on Trapping Performance of Sorbents.

B Silver zeolite, 88% Ag^+ for Na^+ exchange (per analysis at ORNL), 1/8-in. pellets, from Materials Systems Division of Union Carbide Corporation.

C Same material as B.

D Silver zeolite, 26% Ag^+ for Na^+ exchange, 1/16-in. pellets, laboratory-prepared by treating Linde Molecular Sieve Type 13X with $AgNO_3$ solution. (Target degree of exchange was 25%).

E GX135, 8 x 16 mesh (U.S.), silver salt-treated alumina-silica, from North American Carbon Inc.

F Activated carbon, iodized, MSA 85851, 8-14 mesh (Tyler), from Mine Safety Appliances Company.

Table 1. Experimental Details for Long-Term Facility

Each test bed section: two 1-in. deep beds in series, 1.05-in. bed diam.

Test bed temperatures (mean): 66, 100, or 200°C

Superficial off-gas velocities in test beds: 46, 50, or 63 fpm (respectively, for preceding temperatures)

Each collection bed section: three 1-in. deep beds in series, 1-in. bed diam.

Hopcalite bed: 2.6-in. depth, 2.1-in. diam., 350°C, superficial off-gas velocity of 108 fpm

Main air stream: 68 lpm, 1 atm, $\sim$ 85% R.H. (at 26°C)

Target concentrations for continuously injected additives:

NO	1×10^{-5} g/l
Dodecane	2×10^{-6} g/l
I_2	4×10^{-8} g/l (at test bed entrance; equivalent to 5 mg I_2/cm^3 sorbent/yr)

Estimated actual I_2 concentrations (from counting data):

First 77 days exposure	9×10^{-8} g/l
Next 119 days exposure	4×10^{-8} g/l

Periodic CH_3I injection: equivalent to 0.1 mg I/cm^3 sorbent/injection; $\sim 2 \times 10^{-4}$ g CH_3I/l (over $\sim$ 3 min period)

Radioactive labeling:

 I_2 with ^{125}I ($t_{1/2}$ = 60 days) CH_3I with ^{130}I ($t_{1/2}$ = 12.3 hr)

After 77 days of operation, the iodized charcoal without Hopcalite upstream was replaced by GX135, at 100°C, and the 88% silver zeolite (1/8-in. pellets) at 100°C (both positions at 100°C having been involved) was replaced by 99% silver zeolite, 1/16-in. pellets, at 100°C. The latter sorbent is from Union Carbide Corporation.

Then, after 196 days of operation, the iodized charcoal with Hopcalite upstream was replaced by GX135, at 100°C, and the 88% silver zeolite (1/8-in. pellets) at 200°C (both positions) was replaced by 88% silver zeolite, 10 x 20 mesh (U.S.) beads, at 200°C. The latter sorbent is from Davison Chemical Division of W. R. Grace and Company. (Results corresponding to sorbent beds installed after 196 days are not yet available.)

Procedure

Initially, the catalyst (Hopcalite) and sorbents were preequilibrated at their operating temperatures to the flowing humid air for 27 hr without the introduction of additives other than water vapor. (Each time fresh Hopcalite was employed, it was degassed at 350°C prior to connecting its holder with the line leading to the downstream sorbents; whether or not this step served a useful purpose is unknown.) Next, the first methyl iodide injection was performed. Around 17 hr later, the collection beds were removed (and replaced) and assayed for ^{130}I. Then, a few hours after removal of the collection beds, introduction of dodecane, I_2, and NO was initiated. In obtaining subsequent methyl iodide trapping results, a similar procedure was employed except, in addition, the collection beds were assayed for ^{125}I after allowing sufficient time for essentially complete decay of ^{130}I. (The introduction of additives continued undisturbed during this subsequent methyl iodide testing.) While methyl iodide results were obtained for the sorbents initially installed prior to the introduction of dodecane, NO, and I_2, analogous results (i.e., for zero exposure time) were not obtained for the replacement sorbent beds.

The Hopcalite beds were changed out after, referring to successive cases, 77, 63, and 56 days exposure to simulated off-gas.

Evaluation of Decontamination Factors

As already indicated, periodic results are obtained corresponding to the trapping of iodine introduced as CH_3I and its retention for around 17 hr. The results for a particular injection are evaluated without regard to those for a different injection, that is, the methyl iodide results are on a noncumulative basis. Each of the decontamination factors presented herein for methyl iodide and associated with a given 2-in. depth of sorbent corresponds to the following quotient: one tenth the corrected counting rate of the ^{130}I-labeled source, as determined just prior to injection, divided by the sum of the corrected ^{130}I-counting rates found for the parts (beds, screens, and retaining springs) of the collection bed section downstream of that 2-in. depth of sorbent. (The apportionment is one-tenth because there are ten sorbent sections, and the counting rates as used include corrections for decay and background.) The methyl iodide decontamination factors associated with sorbents downstream of Hopcalite are actually manifestations of I_2 trapping capability since the methyl iodide which traversed the Hopcalite bed was converted to elemental iodine. (6) Some fraction of the latter is undoubtedly retained over the time period involved on surfaces upstream of the sorbents. Also, considering the manner in which the methyl iodide decontamination factors are evaluated, any amounts of ^{130}I retained in the connecting lines between the sorbent bed sections and the collection bed

sections are, in effect, included with the quantities trapped further upstream. (The connecting lines are of 1/4-in. O.D., 35-mil wall, stainless steel type 316; lengths are 0.7 ft where sorbent temperatures are 66 or 100°C and 5 ft where sorbent temperatures are 200°C.) Accordingly, each of these methyl iodide decontamination factors corresponds to the overall result of all removal processes occurring between the point of injection and the point of entrance into the applicable collection bed section.

As contrasted with the results for methyl iodide, the decontamination factors for elemental iodine are evaluated on a cumulative basis for the relatively long exposure periods involved and apply, within the limitations to be indicated, to those quantities of ^{125}I-labeled iodine which enter the test bed sections. For each of those cases where the test beds were removed and assayed for ^{125}I, excluding two cases where the associated collection beds were indicative of ineffective trapping, the quantity of iodine entering was taken to be that found on the removed test beds (the two 1-in. depths in series) plus that found on the two or more successive collection bed sections associated with them. (Actually, the calculations were made in terms of corrected counting rates, which included allowance for the different degrees of attenuation by different sorbents, the latter correction being necessitated by the low energy of ^{125}I radiation.(9)) For other cases, the quantities of entering iodine are estimates based on those quantities evaluated as described above, length of exposure time, and the particular time period pertaining (to allow for the variation in effective I_2 concentration). Each I_2 decontamination factor, then, is the quotient of the calculated amount of iodine (injected as I_2) entering the test bed section during the specified exposure time divided by the total amount found on the one or more collection bed sections that was (were) located downstream during that exposure time. Quantities of iodine retained in the lines between the test bed sections and the collection bed sections are not measured and, therefore, the I_2 results are interpreted in a manner somewhat similar to that employed for the CH_3I results, with particular reference being made to the situation where conversion to I_2 by passage through Hopcalite pertained. (For the I_2 results, however, any ^{125}I retention occurring upstream of the sorbents is not directly involved in their interpretation.) Accordingly, each of the I_2 decontamination factors corresponds to the result of removal processes occurring between the point of entrance to the applicable test bed section and the point of entrance to its successive collection bed sections.

The effects of iodine retention on nonsorbent surfaces may not be as important in this work as the above discussion would suggest since available evidence indicates that I_2 is transported through the facility at an appreciable rate. However, at least until more definitive information is obtained, recognition of the possible role of nonsorbent surfaces in achieving the degrees of decontamination as were observed appears necessary.

III. Results and Discussion

In the processing of LMFBR fuel which has cooled for the projected time of 30 days, the iodine isotopes of primary concern will be 8.07-day ^{131}I and 1.7 x 10^7-year ^{129}I, with the ^{131}I being controlling with respect to the degree of retention required. The decay of trapped ^{131}I will mitigate the iodine retention problem since ^{131}I decays to stable ^{131}Xe either directly or via 11.8-day ^{131m}Xe which is in low yield and which is considerably less hazardous than ^{131}I. As indicated earlier, the decontamination factors (DF's) of this investigation do not reflect decontamination resulting from decay. (That is, the extents of decontamination attributable to ^{125}I or ^{130}I decay were, in effect, eliminated by making appropriate corrections.) The DF's as are to be presented for the ^{125}I-

labeled I_2 are for exposure times of $\geq$ 35 days. Thus, in the extension of these values so as to apply to ^{131}I, the imposition of allowances for ^{131}I decay would result in the revised values being substantially larger. (Calculation of such values has not as yet been performed.) With regard to the DF's for the ^{130}I-labeled CH_3I, the time periods pertaining are short, viz., around 17 hr, and, consequently, imposition of ^{131}I-decay allowances would result in only trivial increases in these values.

Observed Decontamination Factors for Iodine and Methyl Iodide

The results for the sorbents initially installed are presented in Figs. 2-6 where the decontamination factors, evaluated and qualified as already described, are plotted versus accumulated exposure time. In instances where the calculated DF's are substantially in excess of 1 x 10^4, the corresponding data points have arrows pointing upward; where incomplete trapping in the collection beds was indicated, the data points have arrows pointing downward.

The performance observed for the type of iodized charcoal that was investigated (Fig. 2) indicates that its useful service life under the conditions which pertained is rather limited. (The extent to which these results might apply to other types of iodized charcoal is not known.) A striking feature of the data is that trapping (and retention) of iodine introduced as I_2 was affected adversely and to a large extent by the use of Hopcalite. This behavior will be referred to again herein. As may be noted, the DF's for iodine injected as methyl iodide for the case of Hopcalite upstream remained high, due to conversion of methyl iodide to iodine, but this good performance was more than offset by the attendant severe loss in trapping efficiency for the iodine injected as I_2. Actually, the use of charcoal in off-gas systems containing oxides of nitrogen is to be avoided because of the danger of combustion, at least at higher concentrations.(10) Iodized charcoal was included in this investigation for purposes of comparison with previous experience.

The results for 88% silver zeolite, 1/8-in. pellets (Figs. 3 and 4) are indicative of no better than fair performance, considering that DF's of 1 x 10^3 or greater are desired. Again, the use of Hopcalite is observed to be detrimental with regard to I_2 trapping, although the results obtained with this sorbent at 100°C are not very conclusive on this point. That the performance of this material was not better is ascribed to the large pellet size. This sorbent was included partly to examine the effect of pellet size and partly because it was the only commercial form of silver zeolite readily available when operation of the facility was initiated.

Excellent performance was observed for 26% silver zeolite, 1/16-in. pellets, at 200°C (Fig. 5). The methyl iodide decontamination factors are all high and those for I_2 are satisfactorily high. In contrast with the behavior exhibited in Figs. 2, 3, and 4, the use of Hopcalite is indicated to have a beneficial effect on the trapping of I_2.

Excellent performance was observed for GX135 at 200°C (Fig. 6) for the case of Hopcalite upstream. For the case of Hopcalite not upstream, however, the results for methyl iodide at 140 and 196 days exposure indicate significant deterioration in capability for trapping iodine in this form. (In an effort to eliminate ambiguity in the succeeding methyl iodide values, the collection bed sorbent for this particular case has been changed to laboratory-prepared 93% silver zeolite, 1/16-in. pellets.) With respect to I_2 trapping, the use of Hopcalite was observed beneficial.
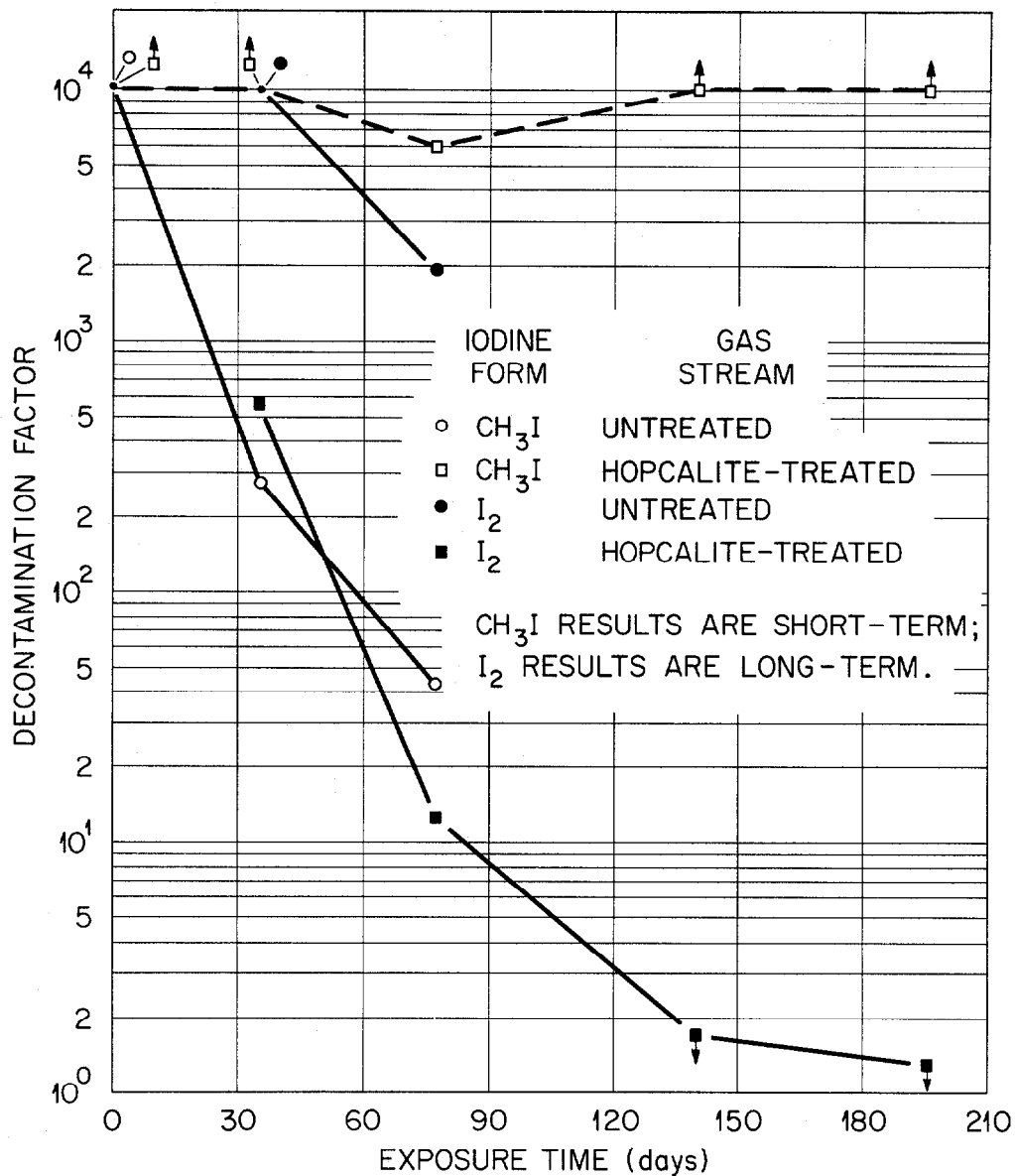
ORNL-DWG 72-8396R

Figure 2. Effect of Exposure to Simulated Off–Gas on Radioiodine Trapping
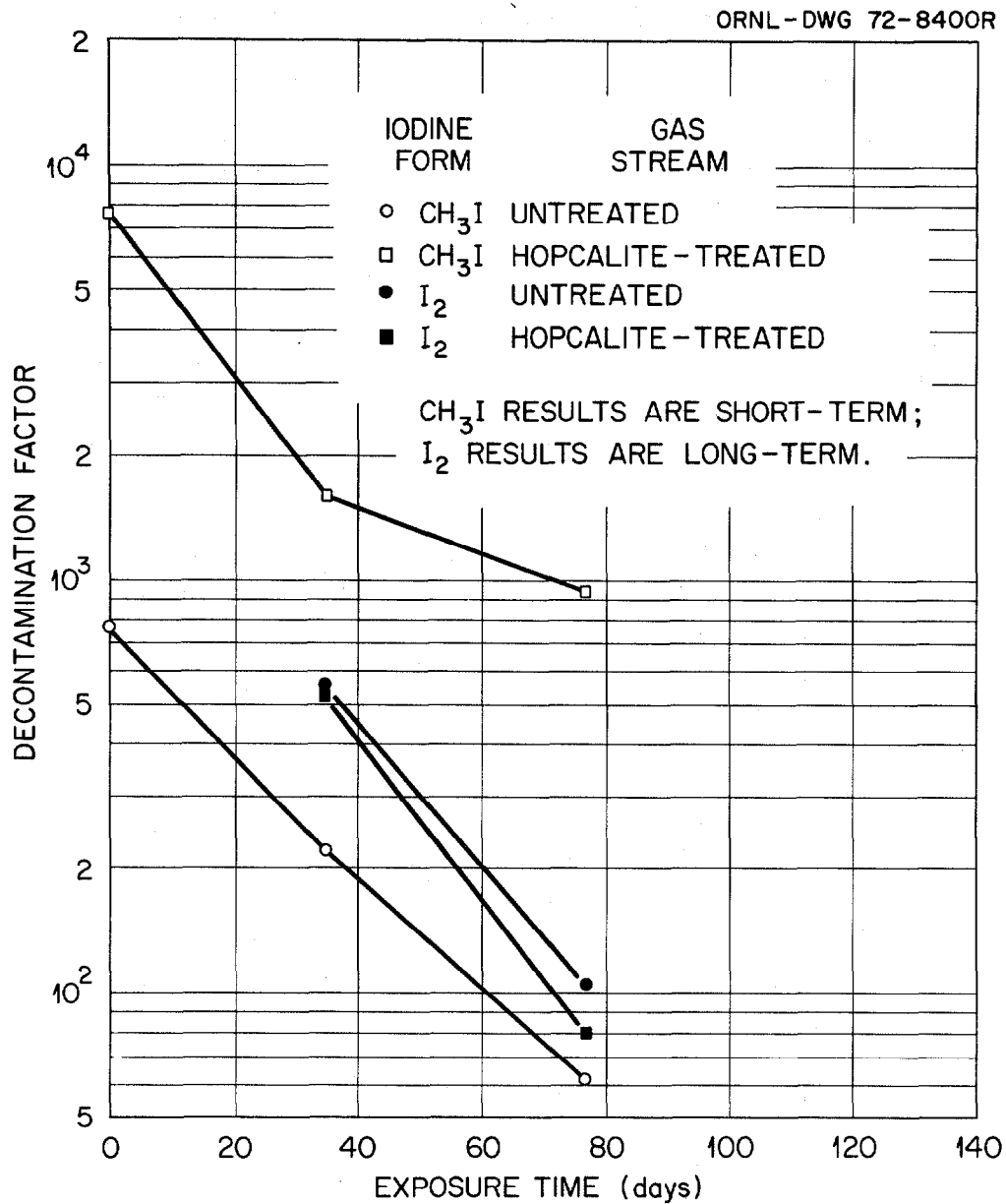Capability of Witco Grade 42 Iodized Charcoal, 8 x 16 Mesh (U.S.), at ∿ 66°C.

Figure 3. Effect of Exposure to Simulated Off-Gas on Radioiodine Trapping Capability of Union Carbide 88% Silver Zeolite, 1/8-in. Pellets, at $\sim$ 100°C.

ORNL-DWG 72-8397R

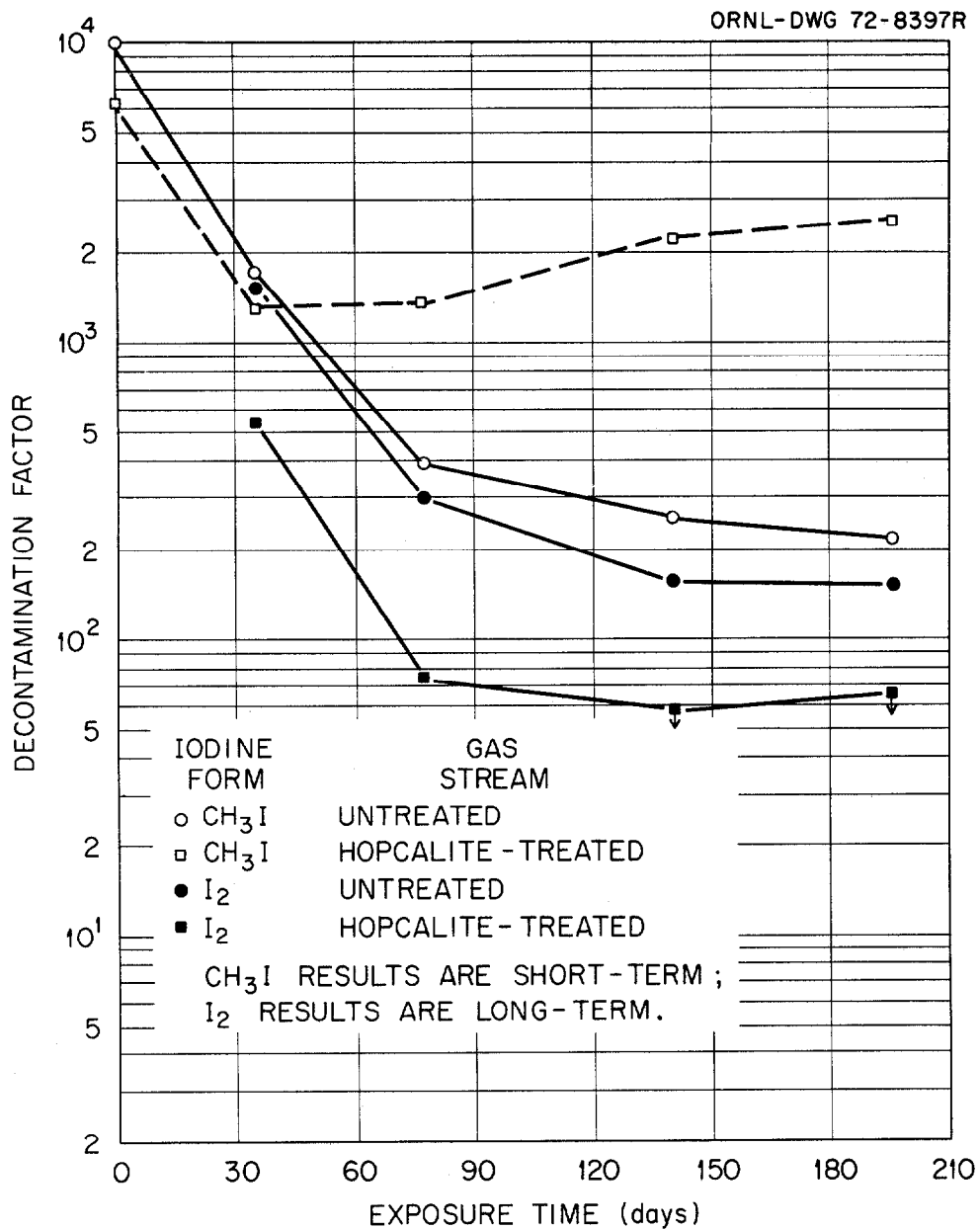

Figure 4.   Effect of Exposure to Simulated Off-Gas on Radioiodine Trapping
Capability of Union Carbide 88% Silver Zeolite, 1/8-in. Pellets, at $\sim$ 200°C.
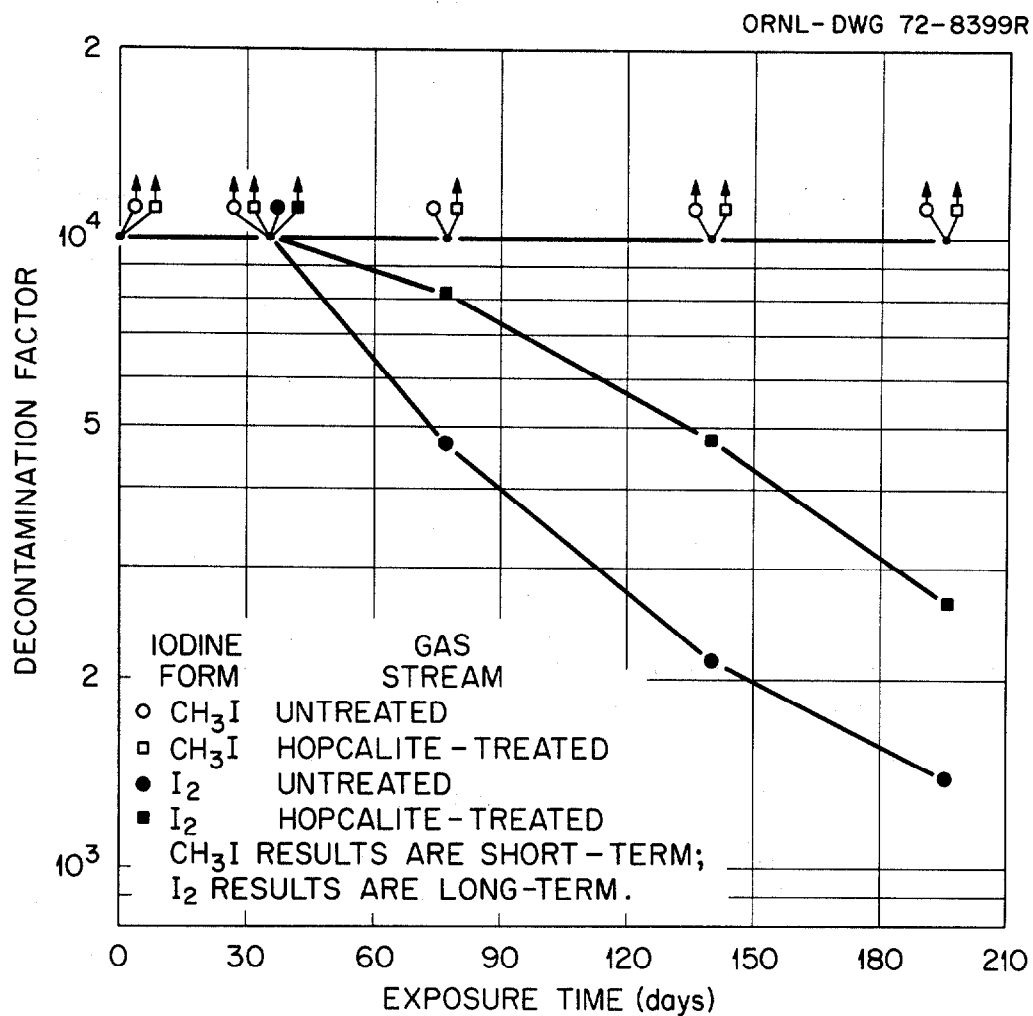
ORNL- DWG 72-8399R

Figure 5. Effect of Exposure to Simulated Off-Gas on Radioiodine Trapping
Capability of Laboratory-Prepared 26% Silver Zeolite, 1/16-in. Pellets, at ∿ 200°C.
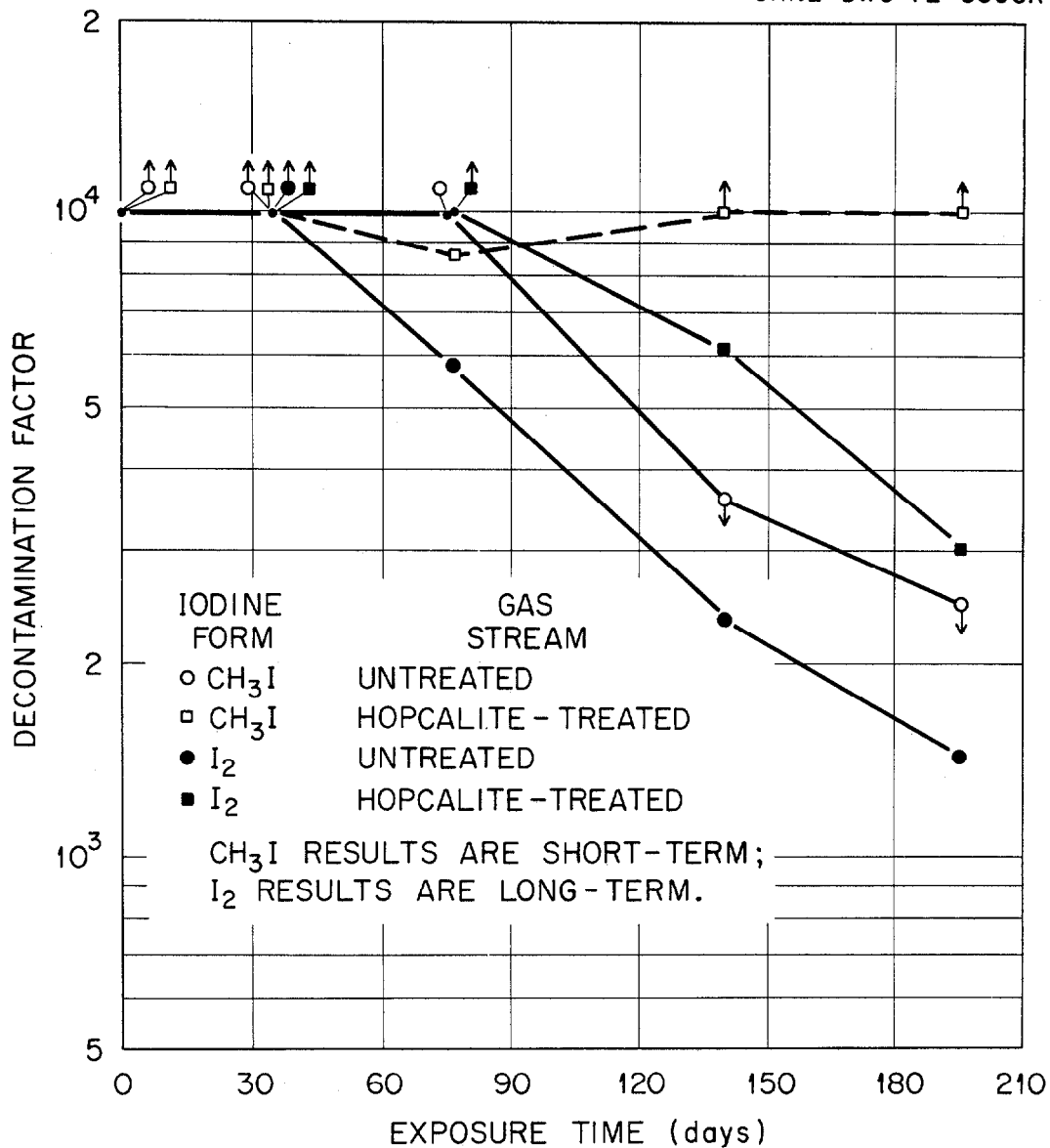
ORNL- DWG 72-8398R

Figure 6. Effect of Exposure to Simulated Off-Gas on Radioiodine Trapping Capability of North American Carbon GX135 (Silver Salt-Treated Alumina-Silica), 8 x 16 Mesh (U.S.), at ∿ 200°C.

The results which have been obtained for the test beds which replaced certain of those initially installed will be described only briefly at this time. The corresponding test situations are the three following: (1) GX135 (from North American Carbon and which is same kind of sorbent as that of Fig. 6), 100°C, without Hopcalite upstream; (2) 99% silver zeolite (from Union Carbide), 1/16-in. pellets, 100°C, without Hopcalite upstream; and (3) like (2) except with Hopcalite upstream. The DF's evaluated for these test situations correspond to exposure times of around 55 and 110 days. Those for CH_3I were all $> 1 \times 10^4$; those for I_2 were all $\geq 1 \times 10^3$. The resolution pertaining to these I_2 DF's was barely adequate due to the corresponding sorbents having been in the facility only during the later part of the overall exposure time, and the ^{125}I activity of the injected iodine had become relatively low. (Modifications in procedure have subsequently been made in order to maintain the ^{125}I activity at a fairly high level and to provide additional data regarding the amount of ^{125}I penetrating to that region of the facility in which the test beds are located.)

Trapping Behavior of Elemental Iodine and Methyl Iodide

Probably, the most notable feature of the results, although not necessarily the most important, was the observation that, for certain of the sorbents, the trapping performance for iodine injected as I_2 was adversely affected by the use of Hopcalite. In this connection, the distribution of ^{125}I in the collection beds is of interest (referring to situations where the collected quantity of ^{125}I was appreciable). For cases where Hopcalite was not upstream, the ^{125}I was trapped effectively in the first of the three collection beds (i.e., like I_2). For the cases where Hopcalite was upstream, significant amounts of ^{125}I were also found in the second and third collection beds. In some of these cases, the successive amounts corresponding to a given set of collection beds decreased in a regular manner as is typical of methyl iodide trapping by iodized charcoal at a relative humidity of, say, 90%. (The reasonable assumption that the distribution is described by a geometric series is employed in calculating and correcting for the radioactivity which penetrates the final collection bed.) In some other of these cases, denoted on the graphs by solid squares with arrows pointing downward, the ^{125}I distribution on the three beds was roughly uniform.

The behavior observed for the ^{130}I-labeled methyl iodide was just the opposite but in accord with expectation. If Hopcalite was not upstream and an appreciable amount penetrated to the collection beds, the ^{130}I was, in general, distributed throughout the collection beds in the descending contour characteristic of the isotopic exchange decontamination process; in two cases, denoted in Fig. 6 by downward arrows, the distribution was roughly uniform. With Hopcalite upstream, that which penetrated the sorbent under test stopped on the first collection bed as a consequence of the conversion from CH_3I to I_2.

Accordingly, the available information indicates that formation of one or more organic compounds of iodine is involved in the poorer performance exhibited by certain of the sorbents with respect to trapping iodine injected as I_2 when the simulated off-gas has traversed the Hopcalite bed. This aspect was investigated by passing portions of the two gas streams, not treated and treated (with Hopcalite), through iodine characterization packs of the type developed by Bennett, Hinds, and Adams. (11) These packs differentiate between reactive iodine (I_2), iodine associated with airborne particles, and organic iodides. The sampling ports were located near the inlets to the test bed sections. At least 98% of the ^{125}I-labeled iodine in either stream was indicated to be in the elemental form. These data together with the related observations are consistent with the following suggested possibilities: (1) that organic fragments in the

Hopcalite-treated stream react with iodine trapped on the test beds to yield organic iodides of which some fraction is evolved and (2) that dodecane in the untreated stream undergoes little reaction with the trapped iodine. These possibilities are not submitted as being on a firm basis, and, perhaps, as the investigation continues, additional evidence, contrary or confirmatory, will be obtained. The feature of the results prompting these comments has not been observed as yet for the more effective sorbents; therefore, from a practical standpoint, the development of a more conclusive interpretation is not regarded as being particularly urgent at the present time.

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DISCUSSION

ETTINGER: In light of the aging effects, will it become necessary to do routine in-place testing of charcoal filters, using methyl iodide, rather than Freon or normal iodine, or to check for effects of weathering or aging?

DAVIS: I think the answer to a question like this depends on how sure you want to be. My feeling is that there is nothing like an in-place test with the material that you really want to stop. We do do in-place testing with both elemental iodine and methyl iodide here at ORNL.

WILHELM: I would like to give an answer to that question, also. We found that it's very hard to see aging effects when testing with elementary iodine because elementary iodine may not be good because of impurities, etc. It's much easier to detect aging effects by testing with methyl iodide. Therefore, to see aging processes, we have chosen methyl iodide as a standard test procedure.